

# **Experimental Investigation, Selection and Thermal Performance Evaluation of Eutectic Mixture Using PCM for Cooking Application**

By

NASIR DETAMO YISHAK



A thesis submitted to

Department of Thermal and Aerospace Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master of Science in

Thermal Engineering

Adama Science and Technology University

Adama, Ethiopia

July, 2019

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## APPROVAL BOARD OF EXAMINERS

We, the undersigned, members of the Board of Examiners of the final open defense by **NASIR DETAMO** have read and evaluated his thesis entitled “**Experimental Investigation, Selection and Thermal Performance Evaluation of Eutectic Mixture Using PCM for Cooking Application**” and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of masters of science in Thermal Engineering.

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### CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the thesis entitled “**Experimental Investigation, Selection and Thermal Performance Evaluation of Eutectic Mixture Using PCM for Cooking Application**” in partial fulfillment of the requirements for the award of the degree of Master of Science in Thermal Engineering is an authentic record of my own work carried out from October 2017 to July 2019 under the supervision of Dr. Dawit Gudeta, (Asst. Prof.) Department of Thermal and Aerospace Engineering, Adama Science and Technology University, Ethiopia.

The matter embodied in this thesis has not been submitted by me for the award of any other degree or diploma. All relevant resources of information used in this thesis have been duly acknowledged.

| Name of candidate | Signature | Date  |
|-------------------|-----------|-------|
| Nasir Detamo      | _____     | _____ |

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief. This thesis has been submitted for examination with my approval.

| Name of advisor   | Signature: | Date  |
|-------------------|------------|-------|
| Dr. Dawit Gudeta, | _____      | _____ |

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## NOMENCLATURE

|                              |                                                   |
|------------------------------|---------------------------------------------------|
| $C_p$                        | Specific heat (J/kg °C)                           |
| $f$                          | Melt fraction                                     |
| $k$                          | Thermal conductivity (W/m °C)                     |
| $L$                          | Length (m)                                        |
| $m$                          | Mass in (kg)                                      |
| $Q$                          | Quantity of heat stored in (J)                    |
| $t$                          | Time (s)                                          |
| $h$                          | Convection heat transfer coefficient              |
| $Z_i$                        | Volumetric ratio                                  |
| $W_i$                        | Mass ratio                                        |
| $X_i$                        | Molar ratio                                       |
| $T$                          | Temperature in (°C)                               |
| $\Delta T$                   | Temperature difference                            |
| $T_{\max}$                   | Maximum temperature                               |
| $\gamma^l$                   | Activity coefficient of the liquid                |
| $\Delta H_i^{sl}$            | Latent heat of fusion of the pure compound        |
| $R$                          | Ideal gas constant                                |
| $\Delta H_{\text{mix}}^{sl}$ | Resultant enthalpies of the eutectic compositions |
| $\Delta C_p^{sl}$            | Specific heats of the component                   |
| $T_{\text{eut}}$             | Eutectic temperature                              |
| $V$                          | Volume                                            |
| $\beta$                      | Expansion coefficient                             |
| $\Delta V$                   | Change of volume                                  |

### Greek letters

|                     |                                                |
|---------------------|------------------------------------------------|
| $\lambda$           | Latent heat of fusion (J/kg)                   |
| $\rho$              | Density (kg/m <sup>3</sup> )                   |
| $\rho_{\text{mix}}$ | Density of mixture in PCM (kg/m <sup>3</sup> ) |

### **Subscript**

|          |         |
|----------|---------|
| L        | Liquid  |
| m        | Melting |
| s        | Solid   |
| I        | Initial |
| F        | Final   |
| $\infty$ | ambient |

## **Abbreviation**

|       |                                    |
|-------|------------------------------------|
| PCM   | Phase change material              |
| TES   | Thermal energy storage             |
| SHS   | Sensible heat storage              |
| LHS   | Latent heat storage                |
| CV    | Control volume                     |
| LHTES | Latent heat thermal energy storage |

## ABSTRACT

*Household cooking is a major energy intensive activity in most of the Ethiopian homes, and because of inefficient charcoal cooking stoves, it causes a polluting environment to the inhabitants. Hence, the electric heating stoves are rapidly replacing the current charcoal stoves. Due to lack of rain there is an extreme shortage of supply of electricity to homes, and inevitably it has become the need of the hour to provide an alternate clean renewable energy source and storage system for cooking applications. In this study, an experimental work carried out to develop a latent heat storage system consisting of different phase change materials. The theoretical results also validated with the previous research work.*

*In this work, molten salt mixtures were used as latent heat storage material. A thermal energy storage (TES) prototype was built with constant electrical heat input. A series of experiments were done by using this prototype to evaluate best mass proportion of molten salt mixtures.*

*During experimentation 2 kg of molten salt mixture were used, and among all the samples two samples “ $\text{NaNO}_3\text{-KNO}_3$ ” and “ $\text{LiNO}_3\text{-NaNO}_3$ ” displayed melting temperatures of 225°C and 202°C respectively, which are well favorable for cooking applications. During experiments, it was found that, the samples with the mass fractions of “60%  $\text{NaNO}_3$ -40%  $\text{KNO}_3$ ” and “46%  $\text{LiNO}_3$ -54%  $\text{NaNO}_3$ ” displayed promising thermal characteristics. Moreover, charging and discharging time for 2 kg of the above mentioned phase change materials were also carried out. The charging time for the storage sample of ( $\text{NaNO}_3\text{-KNO}_3$ ) is 19.1% faster than ( $\text{LiNO}_3\text{-NaNO}_3$ ) and which took about 30.5 minutes to bring it to 300°C, while the discharging time it needs about 42.5 minutes to bring it to 150°C at the same operating conditions.*

*Moreover, further experiments were conducted to ascertain the amount of PCM and the required thermal energy in the storage tank per day for cooking applications. The results revealed that the amount of energy required for six family members was 0.916kWh energy in order to cook lunch and dinner. Similarly, the corresponding amount of PCM was 8.7 kg.*

**Keywords:** Molten salt, Eutectic mixtu

## **CHAPTER ONE**

### **1. INTRODUCTION**

#### **1.1 Background**

According to Ethiopian Rural Development and Promotion Center (2006) [1], 77% of total energy consumption is covered by firewood and charcoal, 15% is from agricultural residue and the remaining 6% was met by modern electricity and kerosene. In the last decades, the increase in energy demand, resulted in a significant impulse to the development of technologies aimed at energy saving and at the production of energy from renewable sources. There are different Renewable energy sources such as wind, solar, hydro power and geothermal are playing more and more significant role in our energy supply. Because the cheap cost and infinite amount of energy storage inside the resource. The use of renewable energy sources and increased energy efficiency are the main strategies to reduce the dependency of fossil fuels.

The wind energy was use as a clean energy to generate electricity since 19th century. However, this renewable energy source not emphasized due to the cheap price of fossil fuel. According to Manwell, J.F[2], The development of wind energy usage continued and in 1990 the first mega-watt wind turbine was launched, which was viewed as a symbol of shift to large scale wind energy utilization The modern application of wind energy mainly relies on wind turbine. On the basis of aerodynamic, wind turbine generates certain net positive torque on rotating shaft and then converts the mechanical power to electrical power. As an electrical power generator, wind turbine connected to some electrical network to transport the electricity to battery charging utilities, residential power systems and large-scale energy consuming systems. In general, most of wind turbines are small scale and can only generate 10KW electrical power. Only few of the wind turbine systems operate with capacity as large as 5MW. Although the usage of wind energy can reduce the emission of carbon oxide, the noise pollution and high cost limit its large scale application. Since the wind is not transportable, the

electrical energy can only be generated where the wind blows, which also decrease the flexibility of wind energy.

Hydropower is currently the largest renewable energy source for power generation around the world. Hydro electricity generation has had a strong increase over the past 50 years [3], which generate electricity by using the gravitational force of falling or flowing water. These days, there are various ways for the water power application. The most traditional method is to store the water in dam and generate electricity by converting the potential energy; pump storage is a different way to utilize water power and can change its output depending on the energy demand by moving water between reservoirs at different elevations. Although the usage of water power can reduce the emission of carbon dioxide and cost. The drawback of hydro power development is difficult due to a large initial fixed investment cost and environmental concerns. Additionally, hydro power has caused problems for local residents associated with the need to relocate the large populations. As result of that, hydro power technique is not a long-term alternative choice.

Geothermal energy is the energy form generated inside the earth. At the very beginning of the planet formation, a large amount of thermal energy was stored from the radioactive decay of minerals, volcanic activity and solar energy absorption. Because of the temperature difference between the core and the surface of planet, the thermal energy stored inside the earth is driven to the outer surface in the form of heat. This form of renewable energy source can be applied to generate electrical power and heat for industrial, space and agricultural applications. Theoretically, the deposited amount of geothermal energy is adequate to supply the energy consumption in the world. However, most of the geothermal energy is stored deeply near the core of the earth, the deep drilling and exploration of geothermal energy is very expensive and limits the large-scale use of this renewable energy source [4].

Among all the renewable energy sources, solar energy is the most suitable alternative energy for our future life. It is clean, cheap, abundant, without any noise, air pollution, no transportation issue and easy to be obtained anywhere in the earth. The basic resource for all solar energy systems is the sun and all life on the earth depends on solar energy. Knowledge of the quantity and quality of solar energy available at a specific location is of prime importance for the design of any solar energy system. Although the solar radiation (insolation) is relatively constant

outside the earth's atmosphere, local climate influences can cause wide variations in available insolation on the earth's surface from site to site. In addition, the relative motion of the sun with respect to the earth will allow surfaces with different orientations to intercept different amounts of solar energy.

The temperature from solar source is sufficient to provide domestic hot water or home heating, but much higher temperature is necessary to displace fossil fuels for producing electricity or other industrial applications. Thus solar radiation must be concentrated to produce this elevated temperature. There are several different methods to take advantage of the solar energy and all the methods can be distinguished into three groups: solar parabolic trough, solar tower and solar dish. Parabolic trough is constructed by silver coated parabolic mirror and there is a Dewar tube going through the length of the mirror and set on the focal point, all the radiation is concentrated on the tube and transfer by heat transfer fluid to the thermal energy storage unit. Solar tower is used to capture solar energy with thousands of mirrors and focus the concentrated sunlight to the top of the tower which is located in the middle of the heliostats. The thermal energy storage medium within the tower was heated to high temperature and transferred to thermal energy storage tank. The solar dish is built with a large, reflective parabolic dish which concentrates all the received sunlight to one spot. There is normally a receiver located on the focal point and transform the solar energy to other forms of useful energy. The use of solar energy to cook food presents a viable alternative to the use of fuel wood, kerosene, and other fuels traditionally used in developing countries for the purpose of preparing food. Now a day the solar PV applications are increasing in Africa, such as Kenya and Tanzania [5] and the potential in Ethiopia is large [6].

The major factor that limits the use of solar energy for various applications is that, it is a cyclic time-dependent energy source. Therefore, solar systems require energy storage to provide energy during the night and overcast periods, which is as important as developing new sources of energy. The stored energy, which can conventionally be converted into the required suitable level, this is a present challenge to the technologists.

Thermal energy storage (TES) is used to keep thermal energy to be used at a later time. A complete TES process involves at least three steps: charging, storing and discharging Figure 1 [7]. The most important part of the storing step is the storage media. A wide variety of choices

exists, depending on the temperature range and the application. For sensible heat storage, water is a common choice because, among its other positive attributes, it has one of the highest specific heats of any liquid at ambient temperatures. Solids have the advantage of higher specific heat capacities, which allow for more compact storage units. TES using latent heat change can also be used; the most common example of latent heat storage is the conversion of water to ice. The other category of storing heat it is considered through the use of reversible endothermic chemical reactions.

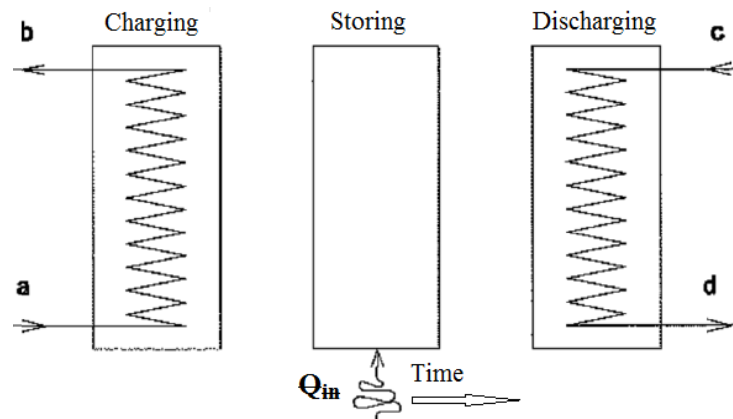


Figure 1. Steps in thermal energy process

Research and development on thermal energy storage (TES) have been conducted in order to obtain a heat storage system with a high heat capacity and good heat transfer mechanism. Determining the appropriate material to store the heat is the key in development of heat storage systems, particularly the investigation of solid–liquid phase change materials (PCMs) due to the following considerations suitable range temperature, involves high latent heat PCMs, narrow phase transition temperature [8].

Researchers suggested the use of thermal energy storage (TES) materials for different application (TES) materials are the materials which stores solar energy in the form of thermal energy. Excess thermal energy can be stored in a several ways; sensible heat, latent heat, or thermochemical. Sensible heat is the storage of heat in the specific heat capacity of a solid or liquid. Latent heat is the storage of heat in the phase change of a material, typically in the solid-liquid transition. Thermo-chemical storage is the storage of heat in a reversible chemical process. Latent Heat Thermal Energy Storage (LHTES) has several advantages over both

thermo-chemical and sensible heat storage. According to Zalba, B., Marin, J [9], presented two main advantages: (i) phase change process is nearly an isothermal process; (ii) it has larger heat storage density with smaller temperature swing. Because the heat required to change phase is typically very large compared to the heat capacity, latent heat storage is significantly more energy dense than sensible heat storage. In addition, more energy is released at a single temperature, which allows the storage system to be optimized for the highest efficiency of the cooking application. Latent heat thermal storage can also include sensible storage in either the liquid or the solid phases, again increasing the amount of heat stored. According to the temperature, the latent heat storage can be divided into three groups: low temperature heat storage ( $<120^{\circ}\text{C}$ ), medium temperature heat storage ( $120\text{--}300^{\circ}\text{C}$ ) and high temperature heat storage ( $>300^{\circ}\text{C}$ ). Many researchers have provided comprehensive reviews of the use of PCMs in solar thermal energy applications for the low temperature and high temperature heat storage [10, 11]. Most of the researchers, however, have not focused on the medium temperature range

Several materials with different melting temperatures investigated, for different application of phase change materials (PCMs). Unfortunately, prior to the large-scale practical application of this technology, it is necessary to resolve numerous problems at the research and development stage. Some of the problems are:

- Phase separation leads to inhomogeneous material distribution, hence the performance of the heat storage changes; all properties vary in the space, and the storage process would be affected;
- Sub-cooling leads to phase change (solidification) at a lower temperature than the expected one, i.e. the temperature of melting; this simply means that the release of energy will appear at a lower temperature;
- Low thermal conductivity is problematic since more time is needed to achieve desired temperature level in the entire material at the same heat flux or for the time given, the temperature in the entire material will not be uniform, and it will significantly vary from the heat source away.

- Phase change temperature is involved the chosen material, which will serve a fixed melting or frizzling temperature range that satisfy the requirements and adequate for the involved operation temperatures

## **1.2 Problem Statement**

Efficient utilization of energy can be achieved by matching the energy supply with demand and by coherent use of thermal energy storage systems. For instance, excess heat generated from a cooking stove can be supplied to thermal energy storage systems, where it can be stored for later utilization during peak demand.

Thermal energy storage uses storage material in order to store heat energy. Different storage materials have own thermal property and storage capacity. In fact, the temperature range is one of the main criteria for the suitability of a PCM for any application. There are numerous thermal energy storage applications that use PCMs; all of them have a particular range suitable for optimal thermal performance. Among all PCMs, molten salt PCMs have a unique opportunity for solar cooking application, due to its unique advantages over other storage materials and hence they are undoubtedly used in the present study. The major drawback of molten salt storage systems is its higher melting point, which limit the application to use in various solar thermal energy storage system. Hence, mixing of molten salt with different type of salt is mandatory to lower its melting point in order to use for required cooking application.

## **1.3 Objectives**

The objective of this study is to develop a molten salt storage system that will utilize the freely available solar energy and become handy for cooking. Specifically, this study focuses on finding the best composition of molten salt mixtures which got the following characteristics:

a) low melting point; b) low charging time, and c) high discharging time.

### **1.3.1 General Objectives**

The general objective is to perform experimental investigations, to select an appropriate PCMs type and, to find the performance evaluation of the developed latent heat thermal energy storage system for cooking application.

### **1.3.2 Specific Objectives**

- Investigating the thermal performance of sodium-potassium, sodium-lithium and lithium-potassium nitrate mixture salt samples with different mass ratio, and its melting points should be lower than existing systems to attain higher efficiency of utilization and with minimal manufacturing expense
- Determine solid–liquid equilibrium of binary eutectics mixtures on prepared samples that are suitable for the cooking application at intermediate temperature (180-230°C).
- Determining the optimum composition mass ratio of storage material mixture and characterized the overall thermal storage performance for cooking application
- Evaluating and comparing the charging/discharging time i.e. analyzing the rate of energy stored/released.

### **1.4 Significance of the Project**

- The majority of people in Ethiopia are living in rural areas, where supply of electricity power is deficit, so this solar storage system helps them in their cooking routine and etc.
- Due to shortage of rainfall this year, major cities of Ethiopia are supplied power on shift basis, and this is creating problem in their daily activities of people. In addition, the main source of cooking in this cities are from electric power, and because of this power cuts this activity is getting disturbed to a larger extent. Hence, the present study is an optimal solution for this problem.

- The conventional way of cooking by burning the wood causes health hazards to women and children of their home. This study provides them a cleaner means of cooking i.e. solar cooking with a storage system.
- The dependency on fuel wood, dung and crop residues emit greenhouse gases and cause air pollution. Hence, the solar cooking systems provides a sustainable solution to all these problems.
- Thermal energy storage systems provide a key method to reduce energy consumption and dependency on fossil fuels.

### **1.5 Limitations of the Project**

Following is the major limitations of my project:

- Based on the previous literature, this study selects three predominant eutectic mixtures namely ‘Sodium nitrate and Lithium nitrate’, ‘Sodium nitrate and Potassium nitrate’ and ‘Potassium nitrate and Lithium nitrate’ for evaluating their performance to find the best mixture composition. Due to rigorous experimentation and fluctuations in power supply other eutectic mixtures were not evaluated.

### **1.6 Organization of the Thesis**

The structure of this thesis work is categorized in to six chapters preceded by the preface of the research which shortly describes the summary of the whole work.

- The first chapter introduces the research paper describing the background of the work, statement of the problem, objectives of the thesis, significance of the thesis and finally limitation of the thesis.
- In the 2 Chapter, reviews of related literatures from books, journals and different websites are offered. The type of storage systems, basics of thermal storage systems and storage material for cooking are discussed. The thermo-physical property of PCM material are described.
- In the 3 Chapter, studies the binary mixture composed of (sodium nitrate with Lithium nitrate), (sodium nitrate with potassium nitrate) and (potassium nitrate with Lithium

nitrate) for use as a PCM for the applications involved. The phase diagram of the system was theoretically determined by mathematical approaches techniques. Their phase diagrams were calculated in order to study whether they form eutectics with melting points suitable for the cooking application ranges. A complete characterization of the main thermo-physical properties of the eutectic composition was performed in order to evaluate its potential as a PCM.

- Chapter 4 deals with the development testing procedure calculation for sizing of LHTES prototype and determining heat loss in order to find storage material mass for the effect of constant heat flux from the electrical heater. The results were first employed to gain knowledge of the system melting and solidification behavior,
- The results and desiccation are analyzed in terms of determination of phase change temperatures at which temperature the storage material will change its phase from solid to liquid and the total energy storage and the time needed for charging and discharging, The thermal properties and crystallization behavior of those compositions
- Finally, the last chapter summarizes the basic findings of the research and conclusions are made. Recommendations based on the research findings of the thesis work are also forwarded in this chapter.

## **CHAPTER TWO**

### **2 LITERATURE REVIEW**

#### **2.1 Introduction**

The intermittent nature of solar energy and its diffused nature need thermal energy storage systems for cooking to be in door and time independent. This chapter discusses the preliminary issues related to this fact. In this chapter reviews of related literature will be discussed. The different methods of thermal energy storage and Comparison between latent heat and sensible heat storage are discussed. Properties, advantages and classification of PCM are present. Development of PCM eutectic mixture Thermodynamic properties molten salts are also reviewed. Finally, the three modes of heat transfer are presented.

#### **2.2 Energy Storage Classification**

The different forms of energy that can be stored include mechanical, electrical and thermal energy its classification have been investigated for the past decades. Sharma [12] classified energy storage methods as follows:

##### **2.2.1 Mechanical Energy Storage:**

Mechanical energy storage systems include gravitational energy storage or pumped hydropower storage (PHPS), compressed air energy storage (CAES) and flywheels.

##### **2.2.2 Electrical storage:**

Energy storage through batteries is an option for storing the electrical energy. A battery is charged, by connecting it to a source of direct electric current and when it is discharged, the stored chemical energy is converted into electrical energy. Electrochemical Energy Storage: battery, fuel cell, electrochemical capacitors and

### **2.2.3 Thermal Energy storage:**

Thermal energy storage can be stored as a change in internal energy of a material as sensible heat, latent heat and thermochemical or combination of these. Thermal Energy Storage is the most widely studied storing concept, where energy is captured and released in the form of heat and later on the thermal energy can be converted to the necessary power. The process of storing energy is called charging and the process of releasing energy from the system is called the discharging process. Thermal energy storage has miscellaneous application starting from producing electricity in small scale to large scale; the storage concept can be applied in waste heat recovery, solar cooker, in building walls and many more [13]. The reason of increasing interest into thermal energy storage (TES) is mostly because loss of energy takes place in the form of heat in the earlier stage of any energy conversion whereas other energy storage concepts are based on the end stage of energy loss. Thermal energy storage system not only increases the power generation capacity but also increases system reliability. It can be applied for solar energy utilization, waste heat recovery, electric appliances with thermostatic regulators and solar cookers. According to Saxena [14] he listed different storage material that can be used for solar cooking application

From the most well-known thermal energy storage, including sensible heat storage and latent heat storage, plays a key role in solar thermal energy. It has been considered as one of the most promising technologies for improving the effective use of available sources of heat when time of generation and demand do not match. The source of all solar energy is the sun and all life on the earth depends on solar energy. Knowledge of the quantity and quality of solar energy available at a specific location is of prime importance for the design of any thermal energy storage system. Although the solar radiation (insolation) is relatively constant outside the earth's atmosphere, local climate influences can cause wide variations in available insolation on the earth's surface from site to site. Thus solar radiation must be concentrated to produce higher temperature; it must also be stored and moved to the point of use

#### **A) Sensible Thermal Storage**

Among the thermal energy storage classification, in case of sensible heat storage, potential of thermal energy stored is less, as stored heat depends on the magnitude of temperature

difference and specific capacity of the storing material. These materials undergo no phase change within the temperature range.

$$Q = mC_p\Delta T \dots\dots\dots (2, 1)$$

One of the best sensible heat storage materials is water because of its uniqueness in terms of high specific capacity, inexpensiveness and availability. But in case of high temperature application soil, molten salts are used. Rock glycol-water or organic liquids are normally used in the heat exchangers for solar collectors, generally Fernandez [15] listed different Selected Materials that used for Sensible Heat Storage are. One of the major disadvantages of sensible heat storage is its low energy density that requires the storage system to be large in volume for high temperature thermal energy storage.

## **B) Latent Heat Storage**

In the latent heat storage concepts, the thermal energy transfer occurs in the form of latent heat, which means when the material is undergoing a phase change. So latent heat storage materials are called the phase change material (PCM). Simone [16] described that PCMs have higher energy density because heat of fusion is much higher for most of the material. It is the most promising heat storage concept in many research studies because of its relatively moderate cost with 5-14 times much higher potential than sensible heat storage and one of the best things of PCMs is it can exhibit isothermally at the melting point unlike the sensible storage system. Studies revealed that liquid-gas transition costs a higher volume for the PCM and solid-solid transition always exhibits low value of latent heat. If isothermal operation at the phase change temperature is difficult; the system operates over a range of temperatures T1 to T2 that includes the melting point. The sensible heat contributions have to be considered and the amount of energy stored is given by:

$$Q = \int_{T_i}^{T_m} mC_p dT + m\lambda + \int_{T_m}^{T_f} mC_p dT \dots\dots\dots (2, 2)$$

where

$Q$  is the total amount of energy stored [J],  $m$  is the mass of the medium [kg],  $C_p$  is the specific heat capacity of the medium at the solid and liquid phase), potentially [J/kg.°C],  $\lambda$  is the latent

heat [J/kg],  $T_m$  is melting temperature,  $T_i$  and  $T_f$  are the initial and final temperatures of the relevant range [K].

### 2.3 Comparison between latent heat and sensible heat storage

**Table 1** shows a comparison between the sensible heat storage using a rock bed and water and the latent heat storage using organic and inorganic compounds. The advantage of the latent heat over the sensible heat is clear from the comparison of the volume and mass of the storage unit required for storing a certain amount of heat. It is also clear that inorganic compounds, such as hydrated salts, have a volumetric thermal storage density, which is higher than that of most organic compounds due to their higher latent heat and density.

Table 1. Comparison between the different methods of heat storage [17]

| Property                           | unit              | rock  | water | Organic PCM | Inorganic PCM |
|------------------------------------|-------------------|-------|-------|-------------|---------------|
| Density                            | kg/m <sup>3</sup> | 2240  | 1000  | 800         | 1600          |
| Specific heat                      | kJ/kg,k           | 1.0   | 4.2   | 2           | 2             |
| Latent heat                        | , kJ/kg           | -     | -     | 190         | 230           |
| Latent heat                        | kJ/m <sup>3</sup> | -     | -     | 152         | 368           |
| Storage mass for 10 <sup>6</sup>   | J, kg             | 67000 | 16000 | 5300        | 4350          |
| Storage volume for 10 <sup>6</sup> | J, m <sup>3</sup> | 30    | 16    | 6.6         | 2.7           |
| Relative storage mass              | -                 | 15    | 4     | 1.25        | 1.0           |
| Relative storage volume            | -                 | 11    | 6     | 2.5         | 1             |

### 2.4 Material properties

A PCM is the heart of any PCM storage system. Having a high latent heat is not the only requirement to use a material as a thermal energy storage material, but also systems should pass desirable thermo-physical, kinetics, chemical and economical properties Zalba. [9] thus, generally, a material is not able to achieve all these requirements.

#### i. Thermal requirements

- Suitable phase-transition temperature to assure store and release of heat at the correct temperature for each application.

- High latent heat of transition to achieve a large storage density in order to minimize the physical size of the heat storage.
- High thermal conductivity to assure storage and release of latent heat in a short time during charging and discharging operation.

**ii. Physical requirements**

- High density to minimize the size of storage container.
- Small volume changes to reduce the containment problem.
- Low vapor pressure to reduce the containment problem.
- Favorable phase equilibrium to assure the stability of the storage capacity during cycles.

**iii. Chemical requirements**

- Chemical stability to avoid degradation after a large number of cycles.
- Compatibility with other materials to avoid problems of corrosion with container.
- Nontoxic, nonflammable and non-explosive behavior for safety and environmental impact.

**iv. Kinetic requirements**

- No sub-cooling to guarantee that melting and solidification take place at correct temperature transition range. The sub-cooling happens when a PCM do not solidify immediately upon cooling below the melting temperature; in this case the crystallization starts only after a temperature well below the melting temperature is reached.

**v. Economics requirements**

- Low price to be competitive with other thermal storage technologies.
- Good recyclability for environmental and economic reasons.

## 2.5 Phase Change Materials Advantage

Phase Change Materials (PCMs) are a latent heat energy storage material that undergo solid-liquid phase transition at specific temperature known as the phase transition temperature. As the PCM material absorbs energy from the surrounding, the material changes its phase from solid to liquid while maintaining nearly constant temperature that corresponds to the phase transition temperature of the PCM. The absorbed energy is stored in the constituent atoms or molecules in the form of vibration energy. When PCM absorbs its maximum energy storage capacity, the atomic bonds are loosened, and the PCM completes its transition from solid to liquid. This amount of energy absorbed during phase transition is known as the latent heat or enthalpy of fusion. Solidification, also known as freezing or crystallization, is the reverse of this process during which the energy is released, molecules are reordered, and the material transitions from liquid to solid at nearly constant temperature. This process can be seen in Figure 2.

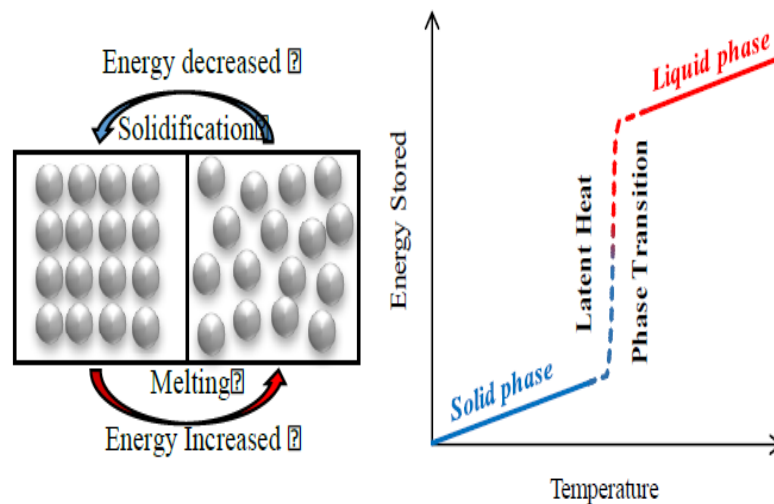


Figure 2. Thermal energy storage process in PCM

When choosing a PCM for a given application the main considerations are the phase transition temperature and the latent heat of fusion. The phase transition temperature needs to be within the operating range of the application, or within the temperature range at which the system needs to be maintained. The latent heat of fusion should be as high as possible. When compared to sensible heat storage materials, Therefore, efficient thermal management is only possible using PCMs, while sensible storage material can only store thermal energy over a

temperature range. Moreover, PCMs have much higher energy storage density, reducing the volume of the system, and resulting in less material mass.

**Kaygusuz, [18]** had conducted an experimental and theoretical study to determine the performance of phase change energy storage materials for solar water-heating systems.  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  was used as phase change material. Simulation techniques are used to determine the system performance over the entire heating season. And he also compared the performance of PCM with water and rock based storage system as shown in figure 3. From his result he concludes that the PCM storage energy stay nearly constant transition temperature during melting and solidification which can be used more preferable as a heat source then the water and rock storage as sensible heat storage materials

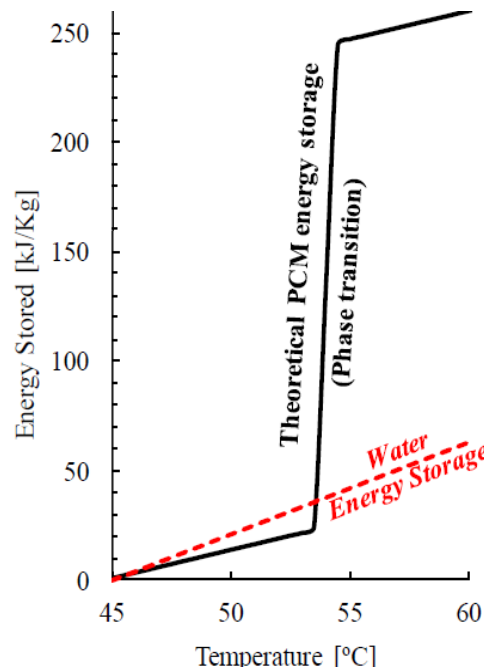


Figure 3. Comparison between thermal energy storage of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (PCM) and water

**Domanski et al. [19]** were the first who used PCM as the energy storage material. They used stearic acid and magnesium nitrate hex-hydrate for energy storage. For this purpose, two concentric cylindrical vessel contracted with 2 cm gape, this gape was filled by PCM. They experimentally evaluated the thermal performance of solar cooker for charging and discharging times of phase change materials. The overall efficiency of about 82% was achieved and maximum temperature inside the cooker was in between 78-84°C. finally they

found that the cooking performance strongly depend on mass of the cooking medium and the thermos-physical property of the PCM. The results obtained are satisfactory which opened the way for further research on PCMs.

**Sharma *et al.* [20]** designed, developed and calculated the thermal performance of box-type solar cooker having latent heat storage unit. To store solar energy during sunshine. The stored energy was utilized to cook food in the evening. They used commercial grade acetamide (melting point 82°C, latent heat of fusion =263 kJ/kg) as PCM. They designed concentric cylindrical vessel for energy storage unit. The void space was filled with PCM. They compared the thermal performance of this cooker with the standard solar cooker. They tested it at different loading conditions. They evaluated from experimental result that evening cooking was possible with solar cooker having the PCM storage unit.

It can be concluded that previous studies concerning on PCM thermal energy storage the systems have recently attracted the attention of researchers because these systems are characterized by a high energy storage density at a constant temperature corresponding to the transition temperature of the phase change material

## **2.6 Classification of phase change material**

PCMs are typically separated into three categories: organic, inorganic, and eutectics. Simone [16] stated the classification of PCM and overview on their properties, advantages and disadvantages of the different classes of PCM, classification is given in Figure 4.

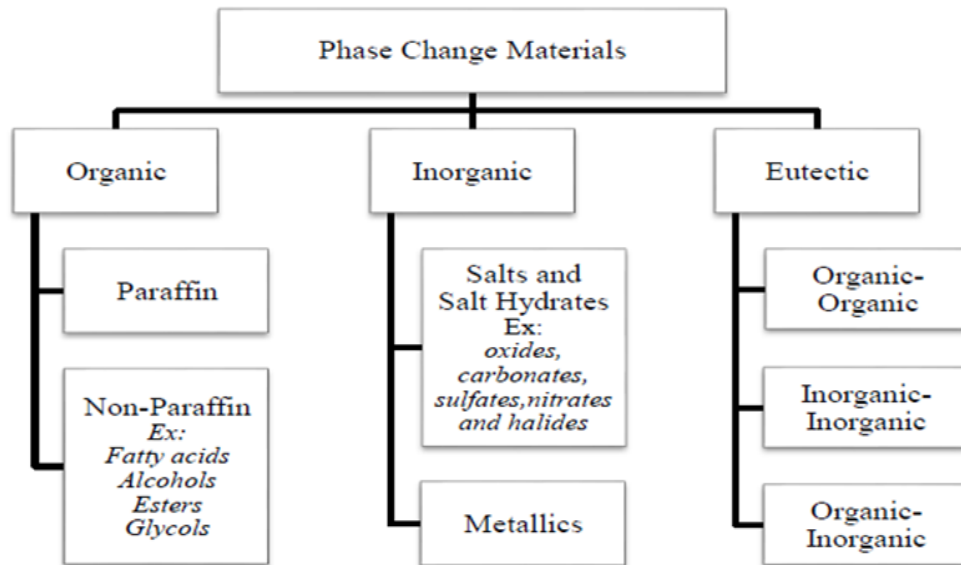


Figure 4. Classification of phase change material

### 2.6.1 Organic PCMs

In general, organic PCMs are the most popular type of PCMs, classified as Paraffin and the non-paraffin. Depending on the hydrocarbon chain structure, each PCM has its particular phase transition temperature and latent heat of fusion. Most organic PCMs are characterized by excellent thermal stability, non-corrosiveness, non-toxicity, and little or no sup-cooling. Their major limitation is the very low thermal conductivity, relatively higher cost, and flammability [16].

#### ➤ Paraffin's

Paraffin wax is the most common organic PCM and consists of a mixture of mostly straight chain n-alkanes  $\text{CH}_3\text{-(CH}_2\text{)-CH}_2$ . Generally, the higher the average length of the hydrocarbon chain, the higher the latent heat of fusion and the melting temperature. Paraffin's are safe, reliable, quite cheap and non-corrosive; others advantages are chemical stability, absence of segregation and sub-cooling, good nucleating and constant thermo-physical properties. However, this material shows some disadvantages such as: low thermal conductivity, high temperature transition range, non-compatible with plastic container, high volume changes

during solid-liquid transition and often is flammable. Table 2 reports examples of paraffin's Use as a PCM

Table 2. Example of paraffin's that have been investigated as PCM [16]

| Material                                                    | Melting temperature [°C] | Melting enthalpy [kJ/kg] | Thermal conductivity [W/m K] |                      | Density [kg/m <sup>3</sup> ] |                    |
|-------------------------------------------------------------|--------------------------|--------------------------|------------------------------|----------------------|------------------------------|--------------------|
|                                                             |                          |                          | <i>solid</i>                 | <i>liquid</i>        | <i>solid</i>                 | <i>liquid</i>      |
| n-Tetradecane C <sub>14</sub> H <sub>30</sub>               | 6                        | 230                      | 0.21                         | -                    | -                            | 760 (liquid, 20°C) |
| n-Hexadecane C <sub>16</sub> H <sub>34</sub>                | 18                       | 210                      | 0.21                         | -                    | -                            | 760 (liquid, 20°C) |
| n-Heptadecane C <sub>17</sub> H <sub>36</sub>               | 19                       | 240                      | -                            | -                    | -                            | 776 (liquid, 20°C) |
| n-Octadecane C <sub>18</sub> H <sub>38</sub>                | 28                       | 200                      | 0.358 (solid, 25°C)          | 0.148 (liquid, 40°C) | 814 (solid, 20°C)            | 774 (liquid, 70°C) |
| n-Triacontane C <sub>30</sub> H <sub>62</sub>               | 66                       | -                        | -                            | -                    | -                            | 778                |
| n-Pentacontane C <sub>50</sub> H <sub>102</sub>             | 95                       | -                        | -                            | -                    | -                            | 779                |
| Polyethylene C <sub>n</sub> H <sub>2n+2</sub> n up to 10000 | 110                      | 200                      | -                            | -                    | 870-940 (solid, 20°)         | -                  |

#### ➤ Non-Paraffin's

The non-paraffin materials are fatty acids, esters, glycols and alcohols and represent the largest category of organic PCM. These materials are flammable and should not be exposed to excessively high temperature, flames or oxidizing agents. Fatty acids have high heat of fusion values comparable to that of paraffin's and also present good cycle stability and no sub-cooling. The disadvantages are corrosiveness, toxicity, instability at high temperature and the cost (2-2.5 times than paraffin). Sugar alcohols have melting temperatures in range between 90°C to 200 °C, present high specific melting enthalpies per unit volume but also sub-cooling. Non-paraffin's are reported in Table 3 (fatty acids), in Table 4 (sugar alcohol).

Table 3. Examples of fatty acids that have been investigated as PCM [16]

| Material                                                               | Melting temperature [°C] | Melting enthalpy [kJ/kg] | Thermal conductivity [W/m·K] |                      | Density [kg/m <sup>3</sup> ] |                    |
|------------------------------------------------------------------------|--------------------------|--------------------------|------------------------------|----------------------|------------------------------|--------------------|
| Caprylic acid<br>CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH  | 16                       | 149                      | -                            | 0.149 (liquid, 38°C) | 981 (solid, 13°C)            | 901 (liquid, 30°C) |
| Capric acid<br>CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH    | 32                       | 153                      | -                            | 0.149 (liquid, 40°C) | 1004 (solid, 24°C)           | 886 (liquid, 40°C) |
| Lauric acid<br>CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH   | 42                       | 178                      |                              | 0.147 (liquid, 50°C) | 1007 (solid, 24°C)           | 870 (liquid, 50°C) |
| Myristic acid<br>CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH | 58                       | 186                      | 0.17 (solid)                 | -                    | 990 (solid, 24°C)            | 861 (liquid, 55°C) |
| Palmitic acid<br>CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH | 61                       | 185                      | -                            | -                    | 989 (solid, 24°C)            | 850 (liquid, 65°C) |

Table 4. Examples of sugar alcohols that have been investigated as PCM [16]

| Material                                                      | Melting temperature [°C] | Melting enthalpy [kJ/kg] | Thermal conductivity [W/m K] |                        | Density [kg/m <sup>3</sup> ] |                      |
|---------------------------------------------------------------|--------------------------|--------------------------|------------------------------|------------------------|------------------------------|----------------------|
|                                                               |                          |                          | Solid                        | liquid                 | solid                        | liquid               |
| Xylitol<br>CH <sub>7</sub> (OH) <sub>5</sub>                  | 94                       | 263                      | -                            | -                      | 1500 (solid, 20°C)           | -                    |
| D-Sorbitol<br>C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub> | 97                       | 185                      | -                            | -                      | 1520 (solid, 20°C)           | -                    |
| Erythritol<br>C <sub>4</sub> H <sub>6</sub> (OH) <sub>4</sub> | 120                      | 340                      | 0.733 (solid, 20°C)          | 0.326 (liquid, 140 °C) | 1480 (solid, 20 °C)          | 1300 (liquid, 140°C) |
| D-Mannitol<br>C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub> | 167                      | 316                      | -                            | -                      | 1520 (solid, 20°C)           | -                    |
| Galactitol<br>C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub> | 188                      | 351                      | -                            | -                      | 1520 lid, 20 °C)             | -                    |

### 2.6.2 Inorganic (PCMs)

Inorganic materials used as PCM are divided into salt hydrate and Metallica's and cover a wide temperature range. Compared to organic PCM, inorganic materials usually have similar melting enthalpies per unit mass, but higher ones per unit volume due to their high density. In general inorganic compounds have almost double volumetric latent heat storage capacity ( $250\text{--}400\text{ kg/dm}^3$ ) than the organic compounds ( $128\text{--}200\text{ kg/dm}^3$ ) [17].

#### ➤ Salt Hydrates

Salt hydrates consist of a water and salt in a discrete mixing ratio. The solid–liquid transformation of salt hydrates is, in fact, a dehydration of hydration of the salt, although this process resembles melting or freezing thermodynamically. Salt hydrates have been widely studied for their use in thermal energy storage systems. There are three different kinds of melting behavior: congruent melting (when the anhydrous salt is completely soluble in water of hydration), in-congruent melting (when the salt is not completely soluble in water) and semi-congruent melting (when the liquid and solid phase is in equilibrium during phase transition). The advantages of this materials are: high latent heat of fusion per unit volume, relatively high thermal conductivity (almost double of the paraffin's), small volume changes during melting process, non-corrosive, compatible with plastics, only slightly toxic and quite cheap. The main drawback is the in-congruent melting. As  $n$  moles of water of hydration are not sufficient to dissolve one mole of salt, the resulting solution is supersaturated at the melting temperature. The solid salt, due to its higher density, settles down at the bottom of the container and the recombination with water during the reverse process of freezing is not possible. This results in an irreversible melting–freezing of the salt hydrate that produce low cycling stability; further more salt hydrate is corrosive with metal containers and present sub-cooling. Table .5 shows examples of salt hydrates used as PCM.

Table 5. Examples of salt hydrates that have been investigated as PCM [16]

| Material                                             | Melting<br>temper<br>ature<br>[°C] | Melting<br>enthalpy<br>[kJ/kg] | Thermal conductivity<br>[W/m K] |                          | Density [kg/m <sup>3</sup> ] |                          |
|------------------------------------------------------|------------------------------------|--------------------------------|---------------------------------|--------------------------|------------------------------|--------------------------|
|                                                      |                                    |                                | solid                           | liquid                   | solid                        | liquid                   |
| LiClO <sub>3</sub> ·3H <sub>2</sub> O                | 8                                  | 155                            | -                               | -                        | 1720 (solid)                 | 1530 (liquid)            |
| KF·3H <sub>2</sub> O                                 | 18.5                               | 231                            | -                               | -                        | 1455 (solid,<br>18°C)        | 1447 (liquid,<br>20°C)   |
| CaCl <sub>2</sub> ·6H <sub>2</sub> O                 | 29                                 | 171                            | 1.088 (solid,<br>23 °C)         | 0.540(liquid,<br>39°C)   | 1710 (solid,<br>25°C)        | 1562 (liquid,<br>32°C)   |
| Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O | 35                                 | 128                            | 0.514 (solid)                   | 0.476 (liquid)           | 1522 (solid)                 | 1442 (liquid)            |
| NaS <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O   | 48                                 | 187                            | -                               | -                        | 1750 (solid)                 | 1670 (liquid)            |
| Na(CH <sub>3</sub> COO)·3H <sub>2</sub> O            | 58                                 | 226                            | -                               | -                        | 1450 (solid)                 | 1280 (liquid)            |
| Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O               | 78                                 | 265                            | 1.255 (solid,<br>23°C)          | 0.653 (liquid,<br>86°C)  | 2180 (solid)                 | 1937 (liquid,<br>84°C)   |
| Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 89                                 | 149                            | 0.669 (solid,<br>56°C)          | 0.49 (liquid,<br>95 °C)  | 1636 (solid,<br>25°C)        | 1550 (liquid,<br>94 °C)  |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O                 | 117                                | 169                            | 0.704 (solid,<br>110 °C)        | 0.57 (liquid,<br>120 °C) | 1569 (solid,<br>20 °C)       | 1450 (liquid,<br>120 °C) |

### ➤ Salt

Above 150 °C, different salts can be used as PCM. The main advantages are very high melting enthalpy, good thermal conductivity, good chemical stability and very low vapor pressure. The main drawbacks are sub-cooling and corrosion of metals. The volume changes from solid to liquid can be up to 10%. Table 6 reports a selection of typical examples.

Table 6. Examples of salt that have been investigated as PCM [16]

| Material                        | Melting temperature<br>[°C] | Melting enthalpy<br>[kJ/kg] | Thermal conductivity<br>[W/m·K] |                  | Density [kg/m <sup>3</sup> ] |                  |
|---------------------------------|-----------------------------|-----------------------------|---------------------------------|------------------|------------------------------|------------------|
|                                 |                             |                             | Solid                           | liquid           | solid                        | liquid           |
| LiNO <sub>3</sub>               | 254                         | 360                         | 1.37 (solid)                    | 0.58<br>(liquid) | 2140 (solid)                 | 1780<br>(liquid) |
| NaNO <sub>3</sub>               | 307                         | 172                         | 0.59 (solid)                    | 0.51<br>(liquid) | 2260 (solid)                 | 1900<br>(liquid) |
| KNO <sub>3</sub>                | 333                         | 266                         | 0.54(solid)                     | 0.50<br>(liquid) | 1900 (solid)                 | 1890<br>(liquid) |
| MgCl <sub>3</sub>               | 714                         | 452                         | -                               | -                | 2140 (solid)                 | -                |
| NaCl                            | 800                         | 492                         | -                               | -                | 2160 (solid)                 | -                |
| Na <sub>2</sub> CO <sub>3</sub> | 854                         | 276                         | -                               | -                | 2533 (solid)                 | -                |
| K <sub>2</sub> CO <sub>3</sub>  | 897                         | 236                         | -                               | -                | 2290 lid)                    | -                |

### 2.6.3 Eutectics (PCMs)

Eutectic materials are a combination of two or more low melting materials with similar (congruent) melting and freezing points. As shown in table 7 eutectics nearly always melt and freeze without segregation and have high thermal conductivities and densities. Eutectic mixtures are used to get new PCMs with improved properties and with different melting temperature. They consist of a mixture of two or more PCM components – organic, or inorganic, or both that melt and freeze simultaneously [21]. Eutectic mixtures are investigated by conducting several experiments until an ideal PCM mixture is found at the required melting temperature with a desirable “sharp” melting behavior and high enthalpy.

Table 7. Examples of eutectics that have been investigated as PCM [22]

| Material          |      | Weight percentage<br>% |       | Melting<br>temperatur<br>e [°C] | Melting<br>enthalpy<br>[kJ/kg] | Specific heat capacity<br>[kJ/kg,k] |        |
|-------------------|------|------------------------|-------|---------------------------------|--------------------------------|-------------------------------------|--------|
| A                 | B    | A                      | B     |                                 |                                | solid                               | liquid |
| KNO <sub>3</sub>  | KCl  | 92.82                  | 7.18  | 307                             | 105                            | 1.156                               | 1.177  |
| KCl               | LiCl | 54.75                  | 45.25 | 352                             | 267                            | 1.009                               | 1.279  |
| FeCl <sub>2</sub> | KCl  | 52.08                  | 47.92 | 350                             | 133                            | 0.706                               | 0.938  |
| KNO <sub>3</sub>  | KBr  | 91.15                  | 8.85  | 329                             | 100.9                          | 1.161                               | 1.161  |

## 2.7 Development of eutectic mixture

Pure PCMs however, do not fully meet the requirements for all thermal energy storage systems. A wide range of technical solutions have been developed. For instance, current existing PCMs are only available at particular phase transition temperatures. PCM mixture is found at the required melting temperature with a desirable “sharp” melting behavior and high enthalpy. Developing a suitable eutectic PCM for cooking applications is very challenging. In this study involves a systematic and rational approach to discover new enhanced energy storage materials that hold promises to achieve a suitable eutectic PCM for cooking applications.

In the solar thermal energy storage applications, PCMs with a melting temperature between 180 °C and 230 °C are great interest for cooking application. If two or more components are found positive results, additional experiments needed to find an optimum mixture and composition, In order to have large amount of heat in this temperature range. The thermal performance of molten salts in this temperature range carried out by researchers. Some researchers focused on developing salt mixtures with medium temperature that could be used as heat storage medium, such as tested by

**Huang [23]** produced the eutectic system of LiNO<sub>3</sub>/KCl heat storage medium and found relatively high latent heat of 178.10 kJ/ kg. They pointed out that the eutectic system has desirable characteristics. However, for use as heat storage material, melting temperature of the eutectics was low. In addition, the other molten salt is Hitec Salt (KNO<sub>3</sub> 53%–NaNO<sub>3</sub>7%–NaNO<sub>2</sub>40%) [24], mostly this salt desirable for HTF because its melting temperature vary low,

whilst, in a latent heat storage system, the molten salts must have a suitable melting temperature (not as low may be better depending on the application temperature) and relatively high latent heat capacity. In addition, other properties such as heat capacity, no phase segregation, low corrosion and low cost thermal expansion, compatibility with other heat storage systems material are also important.

**Zhao et al. [25]** conducted  $\text{Ca}(\text{NO}_3)_2\text{--NaNO}_3$  mixture to determine its potential for latent heat storage applications. They concluded that a mixture of  $\text{Ca}(\text{NO}_3)_2\text{--NaNO}_3$  with a mole ratio of 3:7 demonstrated the best heat storage properties, In terms of its melting point  $217.4^\circ\text{C}$  and heat of fusion  $135.8\text{ kJ/kg}$ .

The nitrate mixtures predominantly applied to be heat storage media for their melting temperature, high latent heat, low unit cost and negligible vapor pressure. The potential nitrate salts with their melting temperatures and latent heats listed in table 6, the  $\text{LiNO}_3$  have relatively high latent heats. However, there is little information in relation to them being use for latent heat storage applications.

It can be concluded that previous studies concerning eutectic mixtures it can be possible to get new PCMs with improved properties and with different melting temperature. Because of the nature of the eutectic mixture, the precise determination of the eutectic composition ratio is very crucial for thermal performance and storage capacity. According to Sarbu, [26] stated the weight percentage of different PCM material need to be varied, to form a new eutectic PCM that melts at the same temperature but with better melting behavior.

Therefore, the eutectic composition for the mixture must be determined in fine steps around the theoretical eutectic point, and experimentally tested over several different composition storage samples; otherwise, an off-eutectic composition will lead to a phase transition separation of the individual components and reducing storage effectiveness. Furthermore, the important thermo-physical properties such as specific heat capacity, thermal conductivity for both liquid and solid phase examined in a detailed manner. Such information is required for modeling the optimum amount, effectiveness, and position of PCMs before being integrated into a thermal system.

## 2.8 Thermodynamic properties of molten salts

Several physical and thermodynamic properties of thermal energy storage materials play significant role in determining the efficiency and performance of solar energy storage systems. In order to evaluate the feasibility of systems, the physic-chemical properties of several molten salts should be reviewed. The three determining parameter which directly affect the thermal energy storage capacity in systems are melting point, heat capacity and density.

There are large amounts of melting point data available in the literature for various molten salt system in previous literatures while those with melting point greater than 254°C. All the previous study on molten salt system revealed that three group of molten salts are emphasized and commonly used: nitrates, carbonates, chloride. Although most of the systems have the same group of cation, the melting point varies a lot from one to another due to the different effect of anions.

### 2.8.1 Melting point

The melting points of salts systems are listed in Table 6 [16]. Among those systems, solar salt  $\text{LiNO}_3$  is the thermal energy storage medium which is currently being used with the melting point of 254°C. Although the melting point for this system is lowest in all the candidate mixtures in this group, the melting points of carbonate systems are different from the nitrate salts, the melting points for carbonate are higher. because of the melting point, the choice of component involved in the carbonate systems is limited. Even though this group of salt working temperature range are relatively high, it is still viewed as possible candidate working at high temperature due to its low price. chloride salts can be also select as one possible choice as the thermal energy storage this group of salt melting points were found in the same range as the carbonate group. And for the pure salt, There are also several systems under organic PCM with the melting points less than 120°C they are not used in the parabolic trough solar power plant due to the decomposition of some components during high temperature.

### 2.8.2 Density

For the solar energy storage system, thermal energy storage density is also essential parameter. The density is needed for the size calculation as function of temperature. Besides, density as function of temperature is used to evaluate the volume change in the process of freezing which contributes to potential stress.

nitrate salts were studied very much about their density as function of temperature. any specific density value in the molten state can be expressed by equation as  $\rho = A - BT$ , where  $\rho$  (g/cm<sup>3</sup>) is the density of salt, A (g/cm<sup>3</sup>) is the initial density value at 0oC and B (mg/cm<sup>3</sup>·°C) is the density change slope as function of temperature. Table 6 showed for the nitrate group molten salts. Among these systems, pure sodium nitrate has the largest value which reveals the high initial density value at low temperature. Conversely, lithium nitrate has the lowest value while it presents the smallest decrease trend as temperature increases [16].

### 2.8.3 Heat capacity

In the heating process, the temperature of solar energy storage molten salt is increase by absorbing energy from the solar radiation. Conversely, the same amount of heat is released and applied to heating system in the process of cooling. Heat capacity is the amount of heat required to increase the temperature of certain material by 1°C and can be viewed as the directly relevant parameter to the energy storage ability. To some extent, the large heat capacity assures the efficiency of the application of solar energy storage materials.

The heat capacity of nitrate salt was presented for system in the previous literature. To simplify the comparison, the heat capacity value at solid and liquid state is shown in the tables 6. Among those nitrate salt systems, lithium nitrate has the largest heat capacity, while potassium nitrate presents the lowest value.

## 2.9 Estimation of thermo-physical property of the PCM

Recent effort has been focused on the development of PCMs for wide range of applications, but a lot of effort has been based on testing new materials rather than targeting limitations of PCMs in general through understanding of the underlying causes. A wide range of energy

storage applications have been proposed using PCMs, from small space heating to the large scale solar cooking applications. In order to develop technical solutions and overcome the limitations of current PCMs, the physics of phase change needs to be fully understood. This sub section is intended to provide a compressive overview of the fundamental conventional measuring mechanism of physical behavior of PCMs, limitations and methods

### **2.9.1 Differential Scanning Calorimeters.**

A Differential Scanning Calorimeter (DSC) is a widely used method to characterize the thermal properties that looks at how a material's heat capacity ( $C_p$ ) is changed by temperature. DSC is used to determine the thermo-physical properties of PCMs such as melting temperature, melting enthalpy. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions such as melts, In DSC analysis, the system measures the difference in the amount of heat required to increase the temperature of a material sample (sample pan) and an empty sample (reference pan) as a function of temperature.

For practical application, a variety of PCMs can be found with a desirable operating temperature range, and high latent heat of fusion. However, there are a number of key factors that must be also considered. The most detailed information about the phase change transition can be obtained from the differential scanning calorimeter (DSC). Different researchers [22, 27, 28], used this method on their experimental study. DSC provide the most comprehensive information about the phase change process. Such as latent heat of fusion, phase transition temperature, phase separation, phase change temperature range, sensible heat component, crystallization, decomposition, sup-cooling and thermal stability. The DSC method is the most reliable and relative accuracy method to characterize the phase transition characteristics of PCMs, but it needs more number of tests, costs and more time than others.

### **2.9.2 Thermo-chemical Software analysis method**

Some of eutectic composition was evaluated using software called Fact-Sage. Using this software, some diagrams can be built based on the thermodynamic stability of different phases. Fact-Sage can also report the minimum temperature at which the liquid phase is stable

(eutectic temperature) and the associated chemical composition for that point (eutectic composition). All the invariant reactions that are occurring are also resolved, as well as their respective compositions and temperatures. All the solid phase will produce 100% of liquid at only one temperature. Another important characteristic that can be considered in selecting PCMs is their congruent melting point. In a congruent melting point, the solid will melt, forming a liquid with the same composition. The pure and intermediate compounds fall in this category [29].

### 2.9.3 Theoretical analysis method

The investigation of eutectic mixtures is usually done by several experiments until an ideal PCM mixture with a certain mass ratio found at a certain melting temperature and high enthalpy. In order to compare the result of the mass percentage, phase change temperature and latent heat of fusion theoretical prediction of phase diagram used.

**Schroeder–Van Laar** equation was employed to calculate the eutectic composition, phase change temperature and latent heat of fusion of binary mixture through theoretical prediction by thermodynamic model using [30, 31,32], Figure 5 shows atypical phase diagram for a binary eutectic PCM. Component A melts at  $T_A$  and component B melts at  $T_B$ . The addition of component A to component B leads to a decrease in the melting temperature along the red line. Similarly, the addition of A to B leads to the same trend. Point E corresponds to the eutectic point of the mixture. At this point both components melt together. Some PCM mixtures do not form a eutectic system, and some of them may form mixtures with a very low latent heat.  $S^A$  and  $S^B$  represent the solid state of components A and B.  $L^A$  and  $L^B$  represent the liquid state of components A and B. L represents a partial liquid state of the eutectic system. Eutectic mixtures are investigated by conducting several experiments until an ideal PCM mixture is found at the required melting temperature with a desirable “sharp” melting behavior and high enthalpy. To have positive results of two components, additional experiments are performed to find an optimum mixture and composition. The mixture at the eutectic point has stable performance and both components crystallize or melt simultaneously. Away from the eutectic molar ratio multiple phase change events may occur at different temperatures and phase separation usually exists.

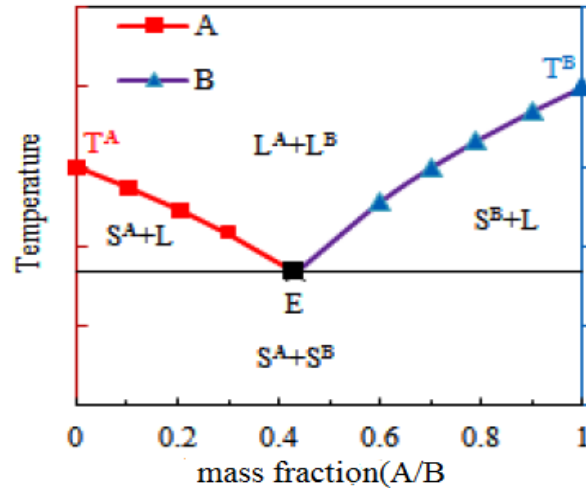


Figure 5. Typical phase diagram for a binary eutectic PCM.

**Bolloso [33]** conducted on binary eutectic mixtures of sugar alcohols for their use as phase change materials (PCMs) in the temperature range suitable for heating and domestic hot water. erythritol and xylitol was used as a binary eutectic mixture, their phase diagrams were experimentally established by differential scanning calorimetry. And he also used A thermodynamics-based modeling approach to compare the theoretical phase diagrams of binary systems. Equilibrium temperatures and melting enthalpies. From the result, he observed good agreement between experimental and theoretical.

Therefore, the thermodynamics-based modeling approach could be used for the prediction of new PCMs made of binary eutectic mixtures. And also the theoretical method helps to reduce the number of experimental test. These classical thermodynamics are applied to resolve phase transitions of molten salt mixtures as well as mixture their composition mass ratio.

## 2.10 Heat Transfer Characteristics in Phase Change Problem

Heat transfer phenomenon in phase change problem is very interesting and worth mentioning. The heat transfer can be conduction, convection or both. Although most researchers agreed on conduction dominant, phase change but convection can also part a significant role when liquid fraction increases or the heat flux. [34]

In most of the cases, convection controlled phase change is selected, when it was assumed that the initial condition of the PCM is in liquid state and waits for solidification. Very few cases

have been found that considered both conduction and convection in the melting time of PCM. However, models based on pure convection or pure conduction could not precisely track down the complex motion of the solid-liquid interface of PCM during melting [34]. to analyze when the shift from conduction to convection heat transfer takes place during phase change melting. few stages of the PCM melting process, which are stated below:

1. Pure conduction takes place when sensible heat increases the temperature of the PCM in the startup period of melting
2. When melting has just begun, the transfer of both sensible heat and latent heat to the solid-liquid interface is also driven by pure conduction.
3. The transition from the conduction to convection takes place when the thickness of the melt layer increases and the interface starts to shift towards the liquid region. This is a transitional regime.
4. The Convection regime is dominant when the most of the interface shifting is maximized and the most of the solid is transferred to liquid

## **2.11 Solar Cookers**

Solar food cookers use an arrangement of reflectors to concentrate solar energy on a cooking vessel. A number of innovative designs have been developed and many of the solar cooker designs are inexpensive and easy to build. Talal, k. [35], he was concluded that the best time for cook with the maximum solar required is between the hours of 11.00 am and 4:00 pm on sunny days and is not possible to cook on cloudy or rainy days or at night unless effective solar storage devices are incorporated.

Direct solar cookers are cookers; in which cooking system uses direct solar energy to cook foods. It is a direct-focusing cooker which uses a reflector to focus sunlight directly onto a cooking pot Direct solar cookers have not been widely accepted due to their limitation to indoor and night use, longer cooking time and higher system price. The other solar cooking is indirect solar cooking, in this case the cooking vessel is physically displaced from the collector and a heat transferring medium is required to convey the heat to the cooking surface. Some especial food needs high temperature such food cannot be possible on solar cookers. However, some researcher introductions in some African countries have improved the energy

security of some households [36]. The acceptance of solar cookers could be increased if indoor, indirect, and any time cooking regardless of the sun's presence is possible. This possibility can be provided by integrating heat storage in the cookers. These cookers are advantageous than the direct cookers because they provide high thermal power and temperatures and allow cooking in indoors using heat storage.

## **2.12 Heat transfer mechanism of cooking**

**Lof [4]** explained the mechanism of cooking as: most of the energy required for cooking is consumed during sensible heating period, while, less heat required for physical and chemical changes involved in cooking. The magnitude of energy required for a specific cooking operation is not always known and it depends on the cooking method used (boiling type, frying, roasting). During cooking, 20 % of heat is consumed in bringing food to boiling temperature, 35 % of heat is spent in vaporization of water and 45 % of heat is spent in convection losses [37]. Therefore, insulating the vessel of cooking and also using a lid can considerably reduce the heat losses.

It should be mentioned here that the sensible heating period depends mainly on the material you cook, in other words, once the contents of the cooking vessel have been sensibly heated up to the cooking temperature, the speed of cooking is independent of heat rate. This means that, the differences in time required to cook.

## **2.13 The possible temperature ranges in cooking system**

The magnitude of energy required for a specific cooking operation is depends on the cooking method used (boiling type, frying, roasting). According to the temperature, the latent heat storage can be divided in to three groups: low temperature heat storage ( $<120\text{ }^{\circ}\text{C}$ ), medium temperature heat storage ( $120\text{--}300\text{ }^{\circ}\text{C}$ ) and high temperature heat storage ( $>430\text{ }^{\circ}\text{C}$ ). Many researchers have provided comprehensive reviews the possibility of solar cooking for the medium temperature range heat storage. Valmiki *et al.* and Muthusivagami [38 - 39] they design and evaluation the performance solar cooking stove which suitable for an indirect type solar cooking system integrated with thermal energy storage system. During the cooking

experiment the indoor stovetop maximum temperature could reach a temperature of 150 °C for cooking application.

Furthermore, during cooking the HTF oil Circulate in the System, but there are losses in pipes, in storage tank and pump housing, this loss through insulation which is dependent upon the internal resistance offered by the storage, pipe line insulation, temperature of the hot surface and the surrounding air. According to, Mekonnen, M, [40] in his experimental measurement he Considered those loss and assume about a safety factor of 1.3 in order to compensate the heat loss, therefore, the phase change temperature inside the storage with assume 20% heat loss is acceptable it would be between 180 and 230°C in addition to that, different researcher was examined that the required temperature to baking Injera is 180 to 220°C [41].

## CHAPTER THREE

### 3 THEORETICAL METHODS AND MATERIALS

#### 3.1 Introduction

In this chapter explains, the overall solar thermal energy storage system with working principle, estimating the required energy to cooking food for average family size, selection and propose eutectic composition composed of nitrate molten salts, developing new PCMs in the desired temperature range with increased storage capacities through theoretical prediction. Finally, estimating the required sample mass in the storage and storage volume in prototype.

#### 3.2 Solar Cooking System Description

The solar powered cooking system uses solar radiation as the source of energy. It uses parabolic trough solar collector (PTSC) to convert the solar radiation in to heat energy. The system is composed of the following elements as can be observed from figure (6) a solar concentrator, a receiver, heat storage tank and heat exchange inside the storage, circulation pump placed in the fluid circuit and heat transfer fluid (HTF). PTSCs are linear focus concentrating solar devices suitable for working in the 150oc – 400oc temperature range [42, 43].

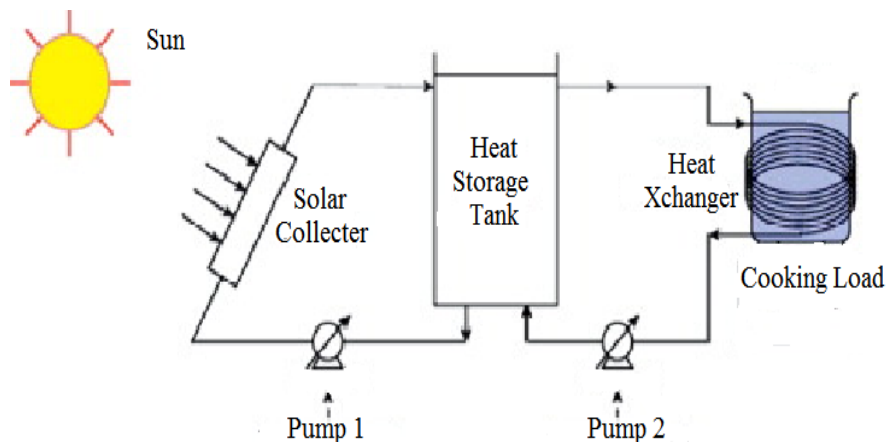


Figure 6. Main components of solar powered cooking system.

### **3.3 Working Principle of storage system**

The working principle of solar powered thermal energy storage cooking System as can be observed from figure (3.1). A parabolic trough is concentrating solar energy on to tube which contains heat transfer fluid (Shell Thermia Oil B) [44]. Thus, heat is transferred from the solar collector to the heat storage unit indirect heating system using heat transfer fluid. Heat transfer fluids circulate in side stationary storage material through heat exchanger, this way of heat storage mechanism known as passive storage. Different heat exchangers have been investigating with the PCM-TES system to evaluate their effectiveness. This proves the significance of using heat exchanger with higher heat transfer area to have a better outcome in terms of heat transfer rate and there will be high charging and discharging rate [45].

In case of charging, heat is transferred from heat transfer fluid (oil) to storage material by convection and conduction heat transfer mechanisms. After giving the energy to the PCM material the oil returned to the absorber through the return pipe line in order to get heated and this circulation continue for the required period of time. When discharging, storage materials releases heat energy and transfer the energy to the end use compartment (cooking pot surface) in order to supply heat energy for cooking. The cooking pan and the heat storage unit are placed separately the heat is transferred indirectly using heat transfer oil. The required temperature in the unit should be equivalent to a standard electric heating plate, which easily and efficiently cook the food or utilize it in other system.

### **3.4 Energy require for cooking**

Cooking requires intensive energy and this energy can be defined as the energy necessary to raise the water to a particular temperature. To measure the energy utilized in cooking, the initial mass of cooking, and the total amount of cooking produced from this cooking were measured.

Thus the mass of water vapor can be obtained by reducing the mass of the cooking produced from the initial mass of cooking. It is assumed that the energy utilized in cooking is the energy required in raising the temperature of the cooking from room temperature to the boiling point of water which is called sensible heat, plus the energy required to evaporate water which is

called latent heat. It is also assumed that the heat capacity of initial cooking material is the same as that of water in order to calculate the energy required to raise the water temperature to boiling point.

Rice cooking requires 76oC [46, 47, 48] and potato require 96oC temperature. In short almost all Ethiopian meal requires at 100oC. Energy required to cook for single lunch and dinner of six member's urban family is 2200.7 kJ which obtained as Equation (3.1).

Therefore, the utilized energy is:

$$E_{utilized} = m_i \times c_{pwater} \times (T_{boil} - T_{room}) + (m_i - m_f) \times h_{vaporization} \dots \dots \dots (3.1)$$

$m_i$  is the mass of expected material for one time, kg,  $T_{boil}$  is the boiling temperature of water, °C,  $T_{room}$  is the room temperature in °C,  $c_{pwater}$  is the heat capacity of water in kJ/kg.k,  $m_f$  is the mass of the produced, kg,  $h_{vaporization}$  is the heat of vaporization of water kJ/kg,  $E_{utilized}$  - Energy utilized in cooking.

### 3.5 Selection method of PCM and their thermal properties

Selection of PCM material is the most preliminary and fundamental step in thermal energy storage design. The selected material based on the ease of availability, low cost for commercial applications, as well as their desirable thermo-physical properties and the most important is melting temperature range, which will serve for cooking application it is around 180-230°C. A comprehensive material investigation has been done reviewing a handsome amount review papers and quality journals a summary of all relevant literature has been already discussed in literature review section.

There are large numbers of phase change materials that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. Paraffin waxes are cheap and have moderate thermal energy storage density but low melting temperature and low thermal conductivity, hence, require large surface area. Hydrated salts have larger energy storage density and higher thermal conductivity but experience super cooling and phase segregation [16].

In contrasts, salts have a long-term stability upon cycling, very high melting enthalpy smaller volume change during phase transition, good thermal conductivity [16]. However, the major limitations of nitrate salts are the sub-cooling, corrosion of metals and that their individual melting temperatures are higher than the required temperature for cooking application. Therefore, eutectic PCM mixtures can be solve this problem, which gives new PCMs with improved properties and new phase transition temperatures.

So, nitrate molten salt PCM are selected to prepared eutectic mixture due to their high energy density, ability to exhibit uniform temperature in isothermal application, thermal conductivity, low cost and availability. Based on this criterion and our specific application requirement, developing a suitable energy storage material for cooking application, the details of selection are explained in Table (8).

Table 8. Thermo-physical property of some pure salt [ 49- 51]

| Comp<br>onents    | Melting<br>point<br>[°C] | Latent<br>heat<br>[kJ/kg] | specific<br>heat<br>(kJ/kg) | specific<br>heat<br>(kJ/Kg) | Price,<br>US<br>(\$/kg) | Thermal<br>conductivity<br>(W/m,°C) | Density<br>(kg/m3)            | Refere<br>nce |
|-------------------|--------------------------|---------------------------|-----------------------------|-----------------------------|-------------------------|-------------------------------------|-------------------------------|---------------|
| LiNO <sub>3</sub> | 254                      | 360                       | 1.306<br>(solid)            | 2.175<br>(liquid)           | 78.5                    | 0.56 (liquid)<br>1.37 (solid)       | 1780 (liquid)<br>2140 (solid) | [16,17]       |
| NaN <sub>3</sub>  | 307                      | 172                       | 1.093<br>(solid)            | 1.686<br>(liquid)           | 14.2                    | 0.51 (liquid)<br>0.59 (solid)       | 1900 (liquid)<br>2260 (solid) | [16,17]       |
| KNO <sub>3</sub>  | 333                      | 266                       | 0.954<br>(solid)            | 1.400<br>(liquid)           | 14.2                    | 0.50 (liquid)<br>0.50 (solid)       | 1890 (liquid)<br>1900 (solid) | [16,17]       |

### 3.6 Preparation of PCM mixtures for the theoretical determination of phase diagrams

The investigation of eutectic mixtures is usually done by several experiments until an ideal PCM mixture with a certain mass ratio found at a certain melting temperature and high enthalpy. In order to compare the result of the mass percentage, phase change temperature and latent heat of fusion theoretical prediction of phase diagram used.

$\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  were the compounds selected for the study. The main characteristics of the used materials can be found in Table 3.1. The theoretical determination was used to calculate the temperature composition phase diagrams of the system. The binary mixtures of ( $\text{NaNO}_3$ :  $\text{LiNO}_3$ ), ( $\text{NaNO}_3$ :  $\text{KNO}_3$ ) and ( $\text{LiNO}_3$ :  $\text{KNO}_3$ ) sample were selected through binary eutectic mixing which used to obtain the new phase change temperature and latent heat of fusion with optimum mass fraction, in order to guarantee an excellent thermal performance. A kind of PCM sample has to possess a high latent heat of fusion and suitable melting temperature with optimum mass fraction in the system. The theoretical determination of binary mixtures sample (A and B) with a series of proportions such as A 90%: B 10%, A 80%: B 20%, A 70%: B 30% ...sample mass ratio were performed. The same mass ratio was done by sharma [52] and he conclude the developed eutectic mixture had good thermal performance.

### **3.7 Modeling of the phase diagrams and calculations**

In this chapter, effort will be made to obtain reliable thermos-physical property of all formulated sample, that is predicted using the theoretical model. A theoretical prediction was used to obtain the phase change temperature, latent heat of fusion, and with optimum mass fraction. These predictive methods can drastically reduce the amount of experimental testing which is required for evaluating PCM candidates. To validate the theoretical results of the eutectic mixtures, comparison can be made from thermochemical software phase diagram result [29],

#### **3.7.1 Phase change temperature**

An approach based on the Gibbs excess energy was adopted to model the solid–liquid behavior of the studied mixtures. thorough explanation of the theoretical background behind the methodology can also be consulted in reference books from chemical thermodynamics, such as ref [33].

The Schroeder–Van Laar equation was employed to calculate the temperature–composition phase diagrams of the systems with melting point and eutectic composition determined simultaneously

, which can be obtained Equation (3.2).

$$x_i \gamma_i^l = \exp((\Delta H_i^{sl}/RT_{mi})((T - T_{mi})/T)) \dots \dots \dots (3.2)$$

There,  $x_i$  indicates the molar fraction of each component;  $\gamma_i^l$  is the activity coefficient of the liquid, which denotes the deviation from an ideal mixture;  $\Delta H_i^{sl}$  represents the latent heat of fusion of the pure compound;  $T_{mi}$  is the melting temperature of the pure compound;  $T$  is the temperature of the system and  $R$  is the ideal gas constant. The subscript  $i$  represents A and B each compound in the system.

### 3.7.2 Latent Heat

The latent heat of fusion for the binary eutectic mixture at the eutectic temperature can be calculated using equation 3.3

$$\Delta H_{mix}^{sl} = \sum_i x_i (\Delta H_i^{sl} + \Delta C_{p,i}^{sl}(T_{mi} - T_{eut})) \dots \dots \dots (3.3)$$

Equation 3.2 used to predict the resultant enthalpies of the eutectic compositions at the eutectic temperature)  $\Delta H_{mix}^{sl}$ . There,  $\Delta C_{p,i}^{sl}$  is the specific heats at constant pressure of the component “ $i$ ” for both the solid and liquid phase and  $T_{eut}$  accounts for eutectic temperature.

### 3.8 Other Thermo-physical properties of eutectic mixtures

Due to the lack of some experimental data to predict thermos-physical properties of eutectic mixtures for missing values, weighting methods techniques have been used [30,31]. Like heat capacity ( $C_p$ ), density ( $\rho$ ) and thermal conductivity ( $\lambda$ ) are presented in equations below. Which use available properties of the mixture and its constituents, molar ratio ( $x_i$ ), mass ratio ( $w_i$ ) to predict the unknown values. Apart from this, we followed the similar calculation techniques for determining the effective Density, capacity heat capacity, thermal conductivity of multi-component nitrate salts,

#### ❖ Density determination

For the solar energy storage system, density for the thermal energy storage material is also essential parameter. The density is needed for the size calculation as function of temperature

and assessing for the thermal stability of thermoclines. Besides, density as function of temperature is used to evaluate the volume change in the process of freezing which contributes to potential stress.

Nitrate salts were studied very much about their density as function of temperature. All the results indicate that the density was decreased linearly as temperature increases and any specific density value in the molten state can be expressed by equation as equation 3.4:

$$\rho = A - BT \dots\dots\dots (3.4)$$

Where  $\rho$  (kg/m<sup>3</sup>) is the density of salt, A (kg/m<sup>3</sup>) is the initial density value at 0°C and B (kg/m<sup>3</sup>.°C) is the density change slope as function of temperature. Other than this a theoretical predicting was also conducted to measure the density of storage material for multi-component nitrite salt systems, Weighting methods techniques have been used The density of the mixed two PCM calculated as equation (3.5).

$$\rho_{\text{mix}} = (x_1 * \rho_{\text{PCM},1}) + (1 - x_1)\rho_{\text{PCM},2} \dots\dots\dots (3.5)$$

#### ❖ Specific heat capacity

In the heating process, the temperature of solar energy storage molten salt is increase by absorbing energy from the solar radiation. Conversely, the same amount of heat is released and applied to heating system in the process of cooling. Heat capacity is the amount of heat required to increase the temperature of certain material by 1°C and can be viewed as the directly relevant parameter to the energy storage ability. To some extent, the large heat capacity assures the efficiency of the application of solar energy storage materials

The heat capacity of nitrate salts were investigated for multi-component system in the previous literature. In the same manner, for calculating the specific heat capacity of storage material weighted average procedure is taken into consideration.

$$C_{p,\text{mix}} = \frac{(x_1 * \rho_{\text{PCM},1} * C_{p,\text{PCM},1}) + (1 - x_1)\rho_{\text{PCM},2} C_{p,\text{PCM},2}}{\rho_{\text{mix}}} \dots\dots\dots (3.6)$$

However, most PCM usually provide low thermal conductivity around 0.5 W/(m·K) [23] The thermal conductivity of nitrate salts were investigated for multi-component system in the

previous literature. In the same manner, for calculating the thermal conductivity of storage material weighted average procedure is taken into consideration. Volumetric ratio ( $Z_i$ ) is required as equation (3.7)

$$Z_i = \frac{w}{\rho_i} \times \left( \left( \frac{w}{\rho} \right)_{PCM,1} + \left( \frac{w}{\rho} \right)_{PCM,2} \right)^{-1} \dots\dots\dots (3,7)$$

$$K_{mix} = K_{PCM,1}^{Z_i} \times K_{PCM,2}^{Z_i} \dots\dots\dots (3.8)$$

The total temperature effect on effective heat capacity has been taken into consideration. Using the same equation for each phase (solid, liquid and mushy), the effective property of the mix PCM of each phase has been derived.

### 3.9 Charging- discharging time determination

The charging and discharging time conducted theoretically by using energy balance during the energy storage on the above measured binary molten salt mixture. For the modeling purpose we need to select some control volumes and implement the energy balance on the molten salt. 700W of heat supplied to the control volume CV, which transfer heat to the (TES) material through conduction heat transfer mechanism.

The heat transfer process between heat supply and PCM storage during charging and discharging processes is analyzed. During charging process, the PCM is receiving heat from the heat source. During discharging process, the PCM is release heat to the food in one direction. And the increase in temperature of the PCM was calculated within every 2-minute Interval until the PCM reaches slightly above its melting point. From the conservation law of energy, we know that:

Energy supplied in CV+ Heat generation inside CV= Energy out of CV + Energy storage in CV

As there is no heat generation and heat loss in our case, we can have our governing equation in 1-D as follows:

$$\rho_s V C_{p,s} \frac{dT_{PCM}}{dt} = \dot{Q} \dots\dots\dots (3.9)$$

The model is based on the following simplifications:

- 1) The PCM is treated as being completely immobile as all natural convection effects are neglected by ignoring
- 2) PCM is as pure material and exhibits a single melting point of in °C
- 3) Thermo-physical properties i.e. specific heat is different from solid to liquid but are not dependent on temperature
- 4) The PCM is homogeneous and isotropic,
- 5) Initial temperature of the latent heat storage unit is uniform and the PCM is in the solid phase for melting or in the liquid phase for solidification,
- 6) No internal heat generation and no radiation effect
- 7) Thermo-physical properties of the PCM are constant,
- 8) The heat source and PCM container walls are very thin so to neglect its thermal Resistance
- 9) Heat transfer to the PCM material constant = 0.7KW
- 10) Initial temperature of PCM is also supposed to be 27°C
- 11) The pressure remains constant during the process

➤ Solid state:

$\ell = 0$  Liquid volume fraction (solid state)

The 1-D model is obtained from Equation (3,10) for the solid phase by considering that the heat conduction occurs only along the one direction. The supplied heat energy is equal to the energy transfer causing the temperature change in PCM, which can be Introducing a finite-difference approximation of the time derivative, and substituting and rearrange the above equation can be written in the following form:

$$T_{PCM}^{m+1} = T_{PCM}^m + \frac{\dot{Q}}{\rho_s V C_{p,s}} \Delta t \dots \dots \dots (3.10)$$

Where:  $m$  is index of the time step,  $\Delta t$  is initial time step (s),  $\rho_s$  is density of solid phase (kg/m<sup>3</sup>),  $V$  is volume of the PCM (m<sup>3</sup>),  $C_{p,s}$  is specific heat of PCM solid phase (J/kg,K),

$T_{PCM}^m$  is the temperature of PCM in time step  $m$  (K),  $T_{PCM}^{m+1}$  is temperature of PCM in time step  $m+1$  (K),  $\dot{Q}$  is the amount of thermal energy stored or released from sensible heat in time (J/s).

#### ➤ Mushy state

In the mushy state the storage material temperature reaches its phase-change level ( $T_{PHM} = T_{melt}$ ). This amount of energy during phase transition is stored in the form of latent heat. The change of enthalpy is caused by the heat obtained from PCM, [46]

There is no temperature change in mushy phase and the first derivative of the temperature is zero: Both the enthalpy and liquid fraction are the function of temperature. As we have taken isothermal phase change, the liquid fraction will be in the range  $\gamma = (0 - 1)$

$$\frac{dT}{dt} = 0 \dots\dots\dots (3.11)$$

The liquid fraction gamma is calculated from Equation (21):

$$\gamma^{m+1} = \gamma^m + \frac{\dot{Q}}{\rho_{PCM} V_{PCM} h_L} \Delta t \dots\dots\dots (3.12)$$

Where:  $h_L$  is the latent heat of PCM (J/kg),  $\rho_{PCM}$  is density of PCM (kg/m<sup>3</sup>),  $V_{PCM}$  is volume of the PCM (m<sup>3</sup>),  $C_{p,PCM}$  is specific heat of PCM (J/kg, K),  $\gamma$  is liquid volume fraction (0-1).

#### ➤ Liquid state

Similarly, as in the case of the heat transfer in the solid state, the heat stored during liquid state, by change of a storage material temperature without phase change. The amount of sensible heat storage is limited by the temperature range of the system as seen in equation 1.

$\gamma = 1$  Liquid volume fraction (liquid state)

$$T_{PCM}^{m+1} = T_{PCM}^m + \frac{\dot{Q}}{\rho_L V C_{p,L}} \Delta t \dots\dots\dots (3.13)$$

Where:  $\rho_L$  is density of PCM at liquid phase ( $\text{kg/m}^3$ ),  $V$  is volume of PCM at liquid phase ( $\text{m}^3$ ),  $c_{p,L}$  is specific heat of liquid phase ( $\text{J/kg, K}$ ).

### 3.10 Sizing of the storage tank

The sample mass and volume of the storage tank was sizing by considering heating rate and thermal expansion of PCM during phase change.

#### 3.10.1 Sample mass and heating rate determination

The governing equation for the heat transfer process within the PCM can be evaluated by applying energy balance to a control surface of the storage. The rate that heat is transferred to the sample is determined from the transient temperature of the constant-power heater in the tube. To get an idea of the quantity of PCM store, evaluate by considering the supplied energy on it that can melt in a required range. Assume, the heat transfer from the heater to the PCM is through conduction heat transfer mechanism only. From the conservation law of energy, we know that.

$$\begin{aligned} &(\text{Rate of heat conduction into control volume} + \text{Rate of heat generation inside control volume}) \\ &= (\text{Rate of heat conduction out of control volume} + \text{Rate of energy storage inside control volume}) \end{aligned}$$

Assumption for the analysis:

- The system is stationary and therefore there is no change of kinetic and potential energy
- The pressure remains constant during the process
- The electric power is supplied continuously for about 40 minutes;
- Assume the thermal property for mixed component of PCM which equivalent to sodium nitrate, thermal conductivity around  $0.51 \text{ W/(m}\cdot\text{K)}$

Applying energy balance to a control surface of the storage tank, from the conservation law of energy we know that [254]. As there is no heat generation in our case,

$$\dot{Q}_{in} - \dot{Q}_{out} = \dot{Q}_{storage} \dots\dots\dots (3.14)$$

In order to calculate heat loss, the overall heat transfer co-efficient should be obtained from the total thermal resistance, It is an indication of resistance to heat flow and is its ability to insulate; the higher the R-value, the better the insulation property will be which is a series combination of thermal resistance, by PCM, PCM wall, ash insulation material and air. A thermal circuit has been shown below to understand the analogy of thermal resistance and electrical resistance in Figure 7.

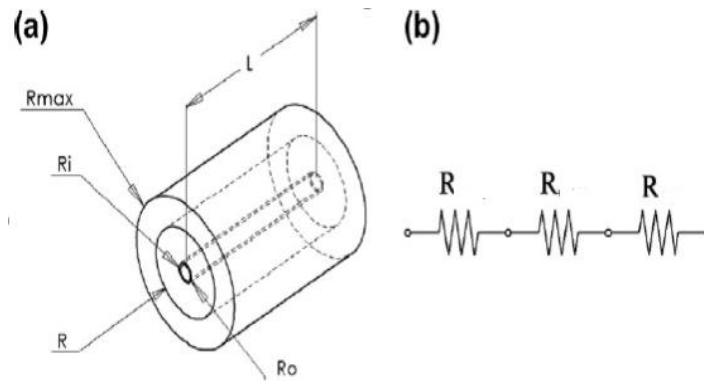


Figure 7. Heat flow from the molten salt to the ambient and its thermal resistance model

The heat loss ( $\dot{Q}_{loss}$ ) can be calculated as follows:

$$\dot{Q}_{loss} = \frac{T_O - T_{\infty}}{R_T} \dots\dots\dots (3.15)$$

$$R_T = \frac{\ln \frac{r_2}{r_1}}{2\pi L k_1} + \frac{\ln \frac{r_3}{r_2}}{2\pi L k_2} + \frac{\ln \frac{r_4}{r_3}}{2\pi L k_1} + \frac{1}{h_1} \dots\dots\dots (3.16)$$

Where

$\dot{Q}_{in}$  Electrical energy supplied by the heater=700W

$T_{max}$  The maximum PCM temperature during heating up process =270.°C

$T_{\infty}$  Ambient temperature =27°C

$k_1$  Thermal conductivity of PCM = 0.51W/m.°C

$t_1$  Thickness of phase change material (PCM) = 0.025m

$k_2$  Thermal conductivity of housing material (carbon steel) = 54W/m.k [40]

$t_2$  Thickness of storage tank sheet metal = 0.002m

- $k_2$  Thermal conductivity of Ash insulating material = 0.14 W/m.k.[48]  
 $t_1$  Thickness of insulating material = 0.04m  
 $h_2$  Convection heat transfer coefficient of ambient air = 10W/m<sup>2</sup>.k[40]

Area (A) exposed to heat loss is:

$$A_{\min} = \pi DL + \frac{\pi D^2}{4} = 0.3266\text{m}^2 \dots\dots\dots (3.17)$$

Thermal resistance ( $R_T$ ) It is a total resistance to heat flow and insulation property, the cylinder consisting of four layers, the thermal resistance is:

$$R_T = \frac{0.4054}{1.036} + \frac{0.01109}{81.012} + \frac{0.2845}{1.0803} + \frac{1}{10} = 3.697 \text{ k/W} \dots\dots\dots (3.18)$$

Applying the equations described below for the heat losses ( $Q_{\text{losses}}$ ), it is then possible to find stored energy by PCM

$$\dot{Q}_{\text{loss}} = \frac{T_i - T_{\infty}}{R_t} = \frac{300 - 27}{3.69} = 74\text{W} \dots\dots\dots (3.20)$$

The energy balance for a given cell

$$\dot{Q}_{in} - \dot{Q}_{loss} = \frac{m[c_{p,s}(T_m - T_{\infty}) + \lambda + c_{p,l}(T_f - T_m)]}{\Delta t} \dots\dots\dots (3.21)$$

The required amount of mass in to prototype

$$m = \frac{(700 - 74)(2400)}{1830(210 - 27) + 110 + 1859(3 - 210)} = 2.1\text{kg} \dots\dots\dots (3.22)$$

Where  $T_m$  is the melting temperature of the eutectic in°C,  $T_{\infty}$  is the ambient temperature,  $T_f$  final temperature  $\lambda$  latent heat of the component at the melting point,  $C_p$  is the difference in heat capacity between the solid and liquid phase.

### 3.10.1 Determination of expansion tank

When the storage tank is subjected to heat, the storage sample will start to expand and tries to displace the space occupied by the air over the sample. An expansion tank is necessary to allow for the change in PCM volume upon heating. The volume of molten salt at 270°C is

about 11.5 percent greater than at room temperature. In this particular case instead of expansion tank the volume of the tank was designed by considering the amount expected to expand at the optimum temperature, so that the tank was large enough to accept the total heat expansion within its own dimensions.

The volume of PCM with change in temperature and the change of volume can be expressed as:  $\Delta V$

$$\Delta V = \beta V_i (T_f - T_i) \dots \dots \dots (3.23)$$

where: -

$\Delta V$ , Change of volume caused by temprature

$V_i$ , Initial volume of molten salt

$\beta$ , Volumetric temperature expansion coefficient = 0.00066 (1/C) [47].

$T_f$ , Final molten salt temperature (°C) =270oC

$T_i$ , Initial molten salt temperature (°C) =27oC

Since the mass of the fluid does not change with temperature, that means the initial volume of the molten salt in the storage at the ambient temperature of 27oC can be calculated from

$$m_f = m_i \rightarrow V_i \rho_i + V_f \rho_f \dots \dots \dots (3.24)$$

Initial volume of the molten salt

$$V_i = \frac{m_{PCM}}{\rho_{PCM}} = \frac{2.1kg}{2080m^3/kg} = 0.001057m^3 = 1.057 \text{ liter} \dots \dots \dots (3.25)$$

change of volume caused by temprature can be expressed as:  $\Delta V$

$$\Delta V = 0.00066 \times 1.057(300 - 20) = 0.2 \text{ liters} \dots \dots \dots (3.26)$$

## CHAPTER FOUR

### 4 EXPERIMENTAL METHODS AND PROCEDURE

#### 4.1 TES prototype system

In order to demonstrate the thermo-physical property of the proposed TES material on salt mixture, a 0.7kW TES prototype has been manufactured and assembled. As shown in figure 8 The supplied energy source is simulated with electrical heating for experimental investigation of the thermo-physical property of PCM. The theoretical results guided the design process to develop the storage prototype for this 0.7 kW TES system. The aim of this chapter is validating the theoretical studies with experimental test. An experimental test system consists of three major components – storage material, storage tank and electrical heater. In addition to this ash insulation and ash wall was included. Experimental tests and manufacture were carried out in the laboratories of (Adama Science and Technology University) on a small scale heat exchanger used as TES device.

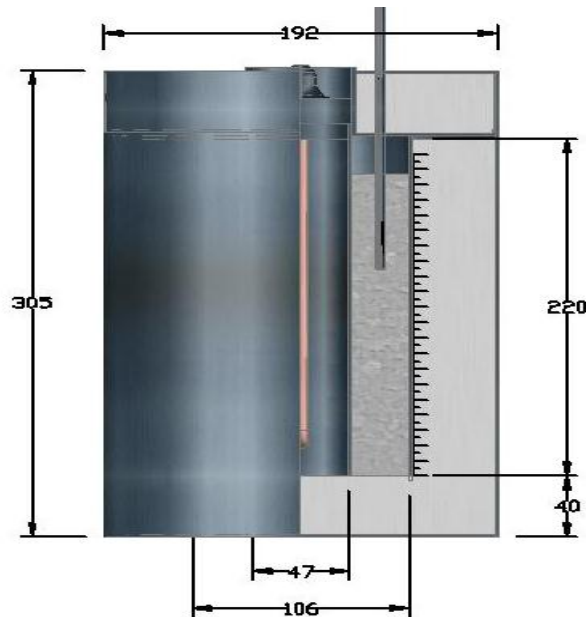


Figure 8. thermal energy storage model.

## 4.2 TES System Assembly

The TES prototype tank is cylindrical in shape, constructed using a three hollow cylindrical tubes made from carbon steel with different diameter that placed one inside the other. The inner cylinder, with a volume of  $397.9 \text{ cm}^3$  has a thickness of 1 mm, a diameter of 0.05 m, and a length of 0.22 m. The second cylinder tank is larger with a thickness of 2 mm, a diameter of 0.11 m, and a length of 0.22 m. The height and volume of the storage tank was designed by considering thermal expansion of the PCM. as shown the schematic assembly system in Figure 8. The inner tube contains electrical heater as a heat source which produce heat and dissipate to the second cylinder in which PCM sample contains. For the purpose of measuring the storage material temperature, k-Type thermocouples inserted at the top of storage System by drilling a small hole through lid and located along the axis of the storage tank at  $x/L = 0.25$ , 0.5 and 0.75 ( $L$  is the length of storage tank in mm and  $x$  is the axial distance from the top of the TES tank in mm) The whole system will be well insulated with over 40mm thick ash in the outer cylinder with a thickness of 1.5 mm to avoid heat loss.

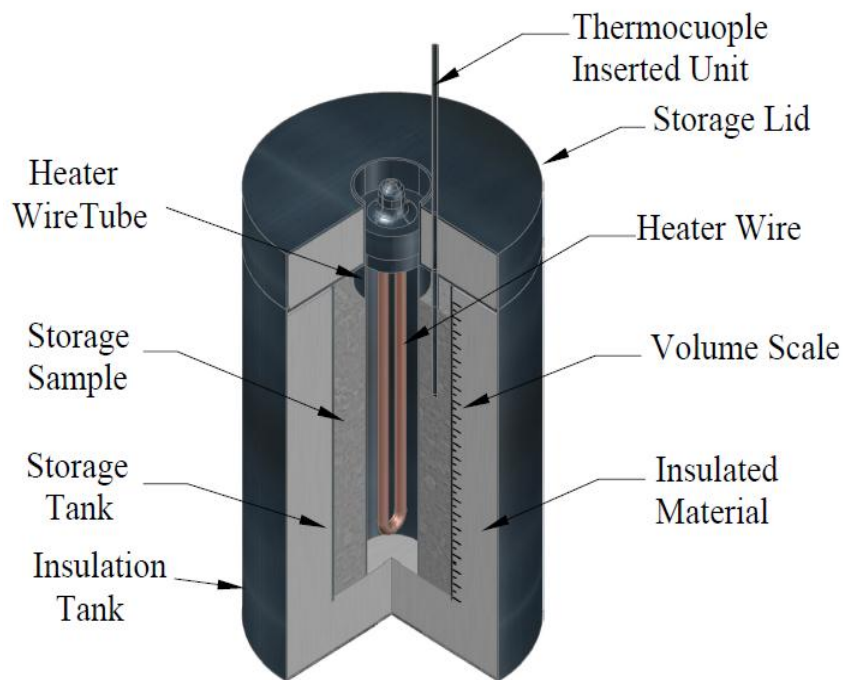


Figure 9. Schematic diagram of TES Prototype System and Assembly

### 4.3 Heat transfer modes

Before the experimental runs, the solid eutectic mixture (2 kg) sample were filled into the storage space in the heat storage unit. It was heated to a high temperature of 270 °C in order to homogenize the mixture. The supply electrical energy was maintained at the constant values of 700W. A typical heat charging run was started at room temperature. The charging run was completed when the temperatures of the thermo-coupled in the eutectic mixture were above the melting temperature range of the eutectic mixture. After the charging, the discharging run was directly by putting 500g of oil in the center. the decrease in temperature of PCM and the increase in oil temperature were recorded with an interval of one minutes. The heat transfer process within the PCM is conduction and convection heat transfer. However, the effect of convection heat transfer within the PCM can be neglected. The different heat losses, which are conduction through insulation material, convection from the outer cylinder to the ambient air.

### 4.4 Preparation of binary mixtures and instruments

The pure material  $\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  were purchased from firmament PLC Addis Ababa manufactured by Blulux laboratory Indian. Their main production specification is shown in Table 9

Table 9. pure materials employed in experimental study

| materials       | Purity | Market price (\$/kg) |
|-----------------|--------|----------------------|
| $\text{LiNO}_3$ | 99 %   | 78.5                 |
| $\text{NaNO}_3$ | 99.5 % | 42.2                 |
| $\text{KNO}_3$  | 99 %   | 42.2                 |



Figure 10. the pure  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  salts

#### ❖ Sample preparation procedure

To produce each formulation, the pure materials were crushed to remove large grains and weighed on ESJ200-4 electrical Balance accuracy  $\pm 0.1\text{mg}$  as shown in figure 11, electronic balance was measured the sample mass with the necessary mass ratio to gate the entire composition range.

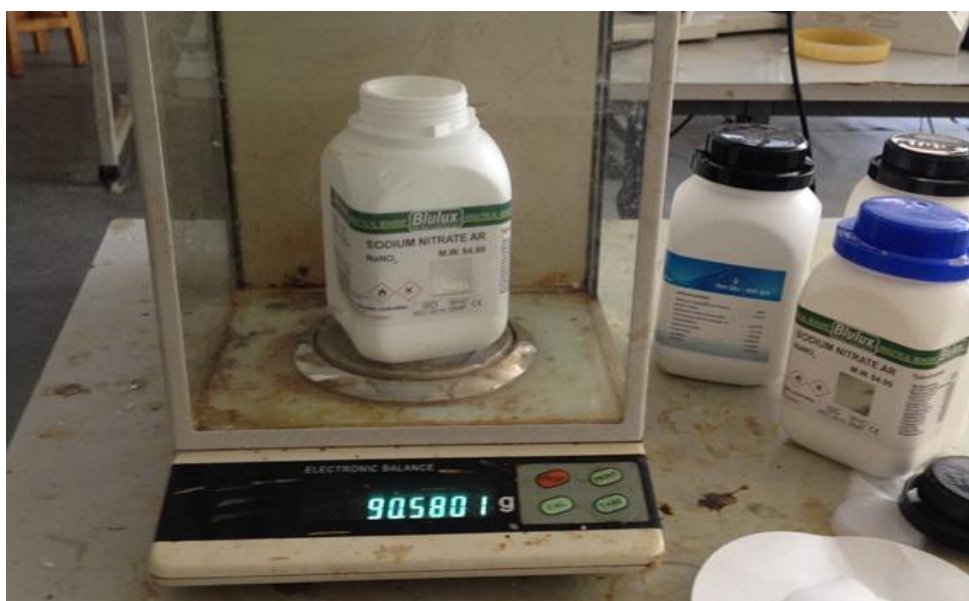


Figure 11. Electrical Balance Machine during preparation

As a result, sample of 2kg physical mixtures were prepared from these pure materials by gentle mixing. The binary mixtures investigated were the following ( $\text{NaNO}_3$ , +  $\text{LiNO}_3$ ), ( $\text{NaNO}_3$ , +  $\text{KNO}_3$ ) and ( $\text{LiNO}_3$ , +  $\text{KNO}_3$ ) samples.

### ❖ Thermocouples

Temperature sensor k-type thermocouples were used during the experimental test to sense the temperature of the storage material and the temperature of the surface. One end of the thermocouple was plugged to the cable from temperature meter and the other end was to the storage material or surface to be measured. The thermocouple measures the radial temperature in the storage material. This type thermocouples temperature range is -270 to 1372°C and the maximum required temperature for this experimental test is 300°C. Therefore, k-type thermocouple can be use.

Before measuring experimental temperature, the measuring device (thermometer) was checked and celebrated by comparing the used thermocouple for this experiment with the other measurements of two different digital thermometers. The calibration procedure was as follow

1. Hot plate is used to warm water to a temperature in a kettle.
2. The thermocouples of our measuring device and the thermometers used for the calibration are dipped into the water.
3. The temperature reading of the measuring device is compared with the temperature readings of the other thermometers.
4. In case of variation, the reset button of the measuring device is used to adjust the measurement so that it can be equivalent with the other readings.

Following this procedure, the calibration of our temperature measuring devise has been done and similar temperature readings has been observed as it is shown in figure 12.



Figure 12. temperature readings of the measuring device (thermometer) and the other two digital thermometers during calibrations.

#### ❖ The Electrical Heater

Electric heater is an electrical appliance that converts electrical energy into heat. The heating element inside every electric heater is simply an electrical resistor, and works on the principle of Joule heating. an electric current through a resistor converts electrical energy into heat energy. From a heat generation standpoint, according to, Sustainable Energy Strategy, 1995 [53] they list out the different energy conversion device with their efficiency, among them Electric heater can be convert 100% electrical energy to heat energy. Electrical heaters were heated a PCM like a traditional heat exchanger by using electrical heat.



Figure 13. The Electrical heater

### ❖ Voltmeter

This meter measures AC/DC Current, AC/DC Voltage, Resistance and Continuity. During the experimental test the voltmeter was used to measure the current and the voltage in order to know and check the power capacity of the electrical heater, and also to measure the continuity of the coils in the electrical heater



Figure 14. Digital multi meter

## 4.5 Thermal energy storage System (TES) Testing

In this study the thermo-physical property of the molten salts was tested by supplying constant heat flux. Electrical heater was utilized to transfer heat from electrical heater wire to the storage material. The testing system consists of three components

- k-type thermocouple was positioned in the midpoint of the storage tank used to monitor the PCM's behavior for testing under controlled experimental conditions. The thermocouple was inserted in the midpoint about 2 cm deep in to the storage material through lid.
- A variable power supply is a device that control the given power. This power converted to the heat through heater wire, power supply use to providing the necessary electrical energy to heater wire, the heater tube was made of stainless steel tube with 50 mm outer diameter and 210 mm length. A nickel-chrome heating wire with 0.2 mm diameter and 50 cm length is used inside the tube and connected to the variable power supply.
- A stop watch uses to control the time range recording the increase in temperature of PCM.

The cylindrical storage sample holder made of carbon steel with 21 cm height and 11 cm inside diameter. The heater wire was energized by the variable power supply with a 0-700 V and 0-200 A (Model GPS-3030DD Good Will) to make heat transfer at radial direction from the heater tube to the surrounding storage sample. The temperature rise was measured by the temperature sensor in the storage sample and recorded at every minute during a period of 40 minutes. A constant power source of 140 V and 5A producing  $700 \text{ W/m}^2$  was found suitable to give a temperature rise of  $270^\circ\text{C}$  from room temperature of  $27^\circ\text{C}$  in. The signals sensed by the thermocouple and transmitted to digital meter.



Figure 15. Experimental setup

1;- Variable power supply, 2;- Power analyzer, 3;- Storage prototype, 4;- Temperature measuring, 5;- Thermocouple, 6;- melt-meter, 7;- time controller,

#### 4.6 Charging and discharging time investigation

The charging and discharging time has been conducted in this experimental test on the PCM, which selected during theoretical analysis. During charging process, the temperature of PCM is increase. The heater wire in the heater tube should be able to melt the storage sample to the temperature of  $270^\circ\text{C}$ . During discharging process 500mL of oil conducted as a load application put it in the heater tube and record the decrease temperature from  $300^\circ\text{C}$  until the PCM temperature reduces to be in order of  $150^\circ\text{C}$  the and the increase in oil temperature

through thermocouple with in every 1 minute interval. The temperatures versus time curves have been plotted in Microsoft excel 2010 on a computer.

#### **4.7 Density Measurements.**

The density of molten salt sample was measured using the volume displacement method. The storage cylinder consists of a 1660 ml graduated measuring scale with 37.7 ml graduation interval with 5mm graduated displacement, (75.4 cm<sup>2</sup> surface area and 220 mm in height). For liquid phase density measurements, sufficient PCM of about 2kg was added to the cylinder and thermocouple inserted in the storage to control the temperature of samples at 300 °C above the melting temperature and at 27°C below melting temperature. When the storage tank is subjected to heat, the salt will start to expand and tries to displace the space occupied by the air gap. Displacement due to volume change over the salt was measured using caliper in order to find the volume change. The volume change was used to calculate the density of solid, liquid and thermal expansion PCM thermal expansion using the equation  $\Delta V = \beta V_0 (T_f - T_0)$

## CHAPTER FIVE

### 5 RESULTS AND DISCUSSION

#### 5.1 Introduction

In this chapter, the detail descriptions of all results are discussed. The discussed results are the characterization of the eutectic mixture using (PCM) on which have a potential for cooking application,

In this section the theoretical phase diagram evaluation of storage samples discussed. Then the experimental result conducted on the given samples, followed by a part dealing with the charging discharging behavior of the materials. The section finishes with a discussion on the experimental determination of the storage performance. During testing on each test were collected for at least two times run to ensure the reproducibility. And the results were plots using Microsoft office excel 2007.

#### 5.2 Theoretical phase diagrams comparison with literature

The phase diagram of the system was carried out using the adopted model explained in chapter three. then, the predicted result compared with the result of the same materials phase diagram which is found in thermo-chemical software called Fact-Sage, as shown in Fig 16. Fact-Sage can report the minimum temperature at which mass fraction of the two pure salts melt simultaneously. The result from Fact-Sage shows eutectic composition of (51%  $\text{NaNO}_3$ - 49%  $\text{LiNO}_3$ ) and (55%  $\text{NaNO}_3$ -45% $\text{KNO}_3$ ) at a melting temperature of 195 °C and 222 °C respectively. The predicted melting points and eutectic composition have good agreement with the literature values. The melting point variation is within 0.58% and 0.39% respectively. And the variation of change of eutectic composition is less than 5.6%and 8.3% respectively. Evaluations of these systems were performed in order to confirm the calculated values. The calculated and software results are displayed in table 11, along with the experimental results obtained.

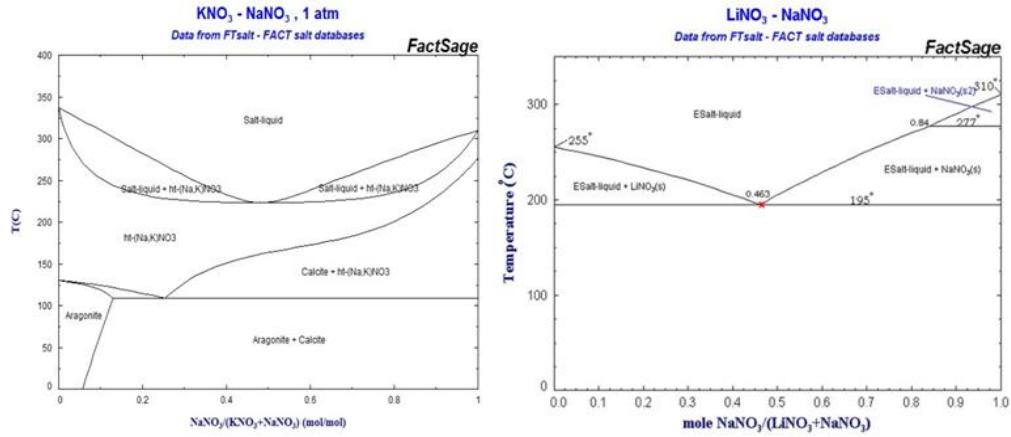


Figure 16. Literature Phase diagrams of  $\text{NaNO}_3 + \text{KNO}_3$  and  $\text{NaNO}_3 + \text{LiNO}_3$

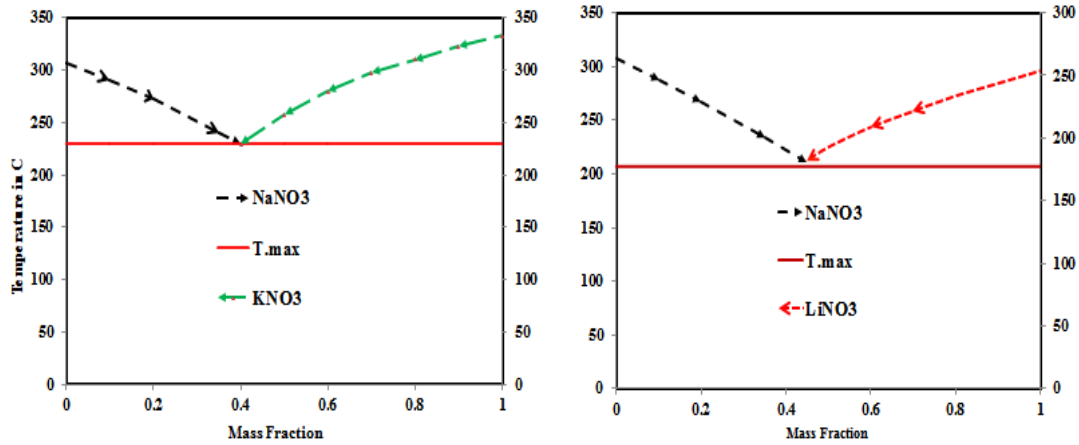


Figure 17. Theoretical phase diagrams of  $\text{NaNO}_3 + \text{KNO}_3$  and  $\text{NaNO}_3 + \text{LiNO}_3$ .

From theoretical and literature results obtained, that the mixtures salt like  $\text{LiNO}_3\text{-KNO}_3$  would not utilized for this application, Lithium nitrate increase the compound cost of salt at the same time of lowering the melting point to around 143°C, which reduce the heat storage capacity in TES system. Moreover, the decreased melting temperature is difficult compared to the temperature that would be used for cooking application due to the decomposition of components during heating. Therefore, this formulation sample is not a good PCM choice for this cooking application. A good PCM should have a melting temperature to be in the range of 180°C and 230°C.

### 5.3 Measuring instrument calibration

Before applying this experimental study instruments need to be calibrated to match their output accuracy with the result that already known. Therefore, pure sodium nitrate was tested for three heating cycles as shown in table 10. From the tests, it was observed the average melting point of pure nitrate salts have good agreement with the literature values that shown in table 6. The variation of melting point is within 1.3%.

Table 10. Calibration data of melting points with different Literature result

| Sample<br>( NaNO <sub>3</sub> ) | Literature<br>T <sub>mp</sub> /(°C) | Experimental.<br>T <sub>mp</sub> /(°C) |
|---------------------------------|-------------------------------------|----------------------------------------|
| 1 <sup>st</sup> , cycle         | 307                                 | 316                                    |
| 2 <sup>nd</sup> , cycle         | <<                                  | 312                                    |
| 3 <sup>rd</sup> , cycle         | <<                                  | 306                                    |
| average                         | 307                                 | 311                                    |

### 5.4 Experimental determination of melting temperature

Two molten salt formulations NaNO<sub>3</sub>–LiNO<sub>3</sub> and NaNO<sub>3</sub>–KNO<sub>3</sub> were tested for melting temperature of the eutectic composition and results derived from the Experimental test on a prototype were performed, as shown in Figure 18. Experimental curve showed how the temperature field of PCM is changing with time by the effect of constant heat flux from the electrical heater. It is clear from the experimental curves that in the solid zone the temperature field is affected only by sensible heat. At the melting point, latent heat is absorbed to breakdown the molecular bond for heating process and the temperature again begins to rise by the effect of sensible heat.

From the figure the first cycle of 60% NaNO<sub>3</sub>-40% KNO<sub>3</sub> formulation sample shows a higher melting point. it represents the melting of the powder mixture in which the stable phases are not yet formed and the melting of the individual components require more energy. Once it is melted, it is expected that the formulation becomes homogeneous and its subsequent melting will resolve its real melting point.

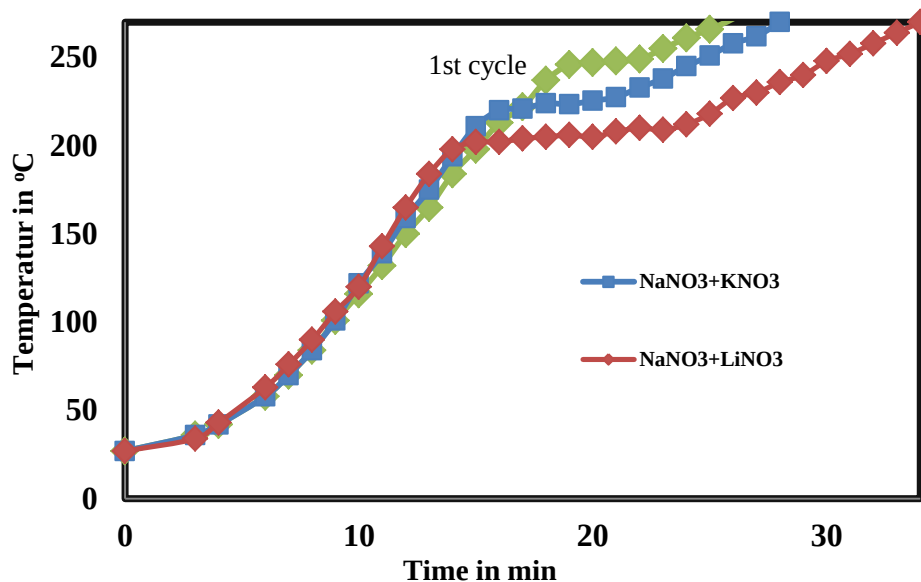


Figure 18. The temperature-time response during melting proces

The temperature-time curve is a key factor in describing maximum melting point of PCMs, as shown in figure 16. The experimental heating process on the two PCM samples, initially the temperature of the PCM was at 27°C. From temperature-time curve the temperature increases gradually on both materials, but the increase rate was lower during initial heat up time and it increases steeply until it reaches the melting point within 15 minutes and stays there at almost constant temperature for 10 and 5.4 minutes since it is a phase change process. The heating process is continued until the PCM temperature becomes in order of 270°C, which is about 69°C, and 45°C greater than that of NaNO<sub>3</sub>-LiNO<sub>3</sub> and NaNO<sub>3</sub>-KNO<sub>3</sub> PCM melting point. The melting process of two formulation samples started with an average solidus temperature or beginning of melting at 196°C and 220°C respectively. The end of melting occurred at an average liquids temperature of 208°C and 230°C. The melting process occurred in a temperature range of about 12°C and 10°C respectively.

Therefore, in our experimental investigation the melting point of two formulations (54% NaNO<sub>3</sub>-46% LiNO<sub>3</sub>) and (60% NaNO<sub>3</sub>-40% KNO<sub>3</sub>) mass ratio samples are 202 °C and 225 °C as it is very close to the results found by theoretical prediction, as can be seen table 5.2. The phase change temperature result between experiments and theoretical showed an absolute maximum difference of 6 °C and 5 °C. The great agreement between experimental and

calculated data verifies the accuracy and feasibility of the storage system This is to address the thermal potential of both mixtures for latent heat storage.

Table 11. Experimental results of melting point comparison with literature and predicted

| Composition<br>salts          | Sample<br>Mass ratio. | Calculated.<br>$T_{mp}/(^{\circ}\text{C})$ | Experimental.<br>$T_{mp}/(^{\circ}\text{C})$ | literature<br>Mass ratio | Literature<br>$T_{mp}/(^{\circ}\text{C})$ |
|-------------------------------|-----------------------|--------------------------------------------|----------------------------------------------|--------------------------|-------------------------------------------|
| $\text{NaNO}_3\text{-LiNO}_3$ | (54-46)               | 207                                        | 202                                          | (51-49)                  | 195                                       |
| $\text{NaNO}_3\text{-KNO}_3$  | (60-40)               | 230                                        | 225                                          | (55-45)                  | 222                                       |

### 5.5 Dependence of melting point on pure and multi components

In the solid state, the movement of individual molecule is holding the material together due to the effect of bonds. However, in the liquid state, the material is disordered due to the breakdown and reforming of the bonds. On the basis of the different conditions of materials in different phases, it can be concluded that the melting process is mainly associated with breaking of material bonds.

Take  $\text{NaNO}_3\text{-KNO}_3$  molten salt, the melting point of pure  $\text{NaNO}_3$  salt is  $317^{\circ}\text{C}$  and the melting point of pure  $\text{KNO}_3$  is  $333^{\circ}\text{C}$ . Based on the simple weighting method rule, the calculated melting point for the binary system is  $323.4^{\circ}\text{C}$ , while experimental melting point is  $225^{\circ}\text{C}$ . The approximate 30.4% difference between these two values is originated from the weakening of material bond when using a mixture of two salts. The weakened material bond results in smaller force to hold material together. As a result of that, lower melting point is obtained for this binary system. Similar phenomenon was observed for  $\text{NaNO}_3\text{-LiNO}_3$  binary mixture the simple weighting method rule, the calculated melting point  $282.6^{\circ}\text{C}$ . And their experimental melting point found  $202^{\circ}\text{C}$ . The approximate difference between the pure and binary mixture of this nitrate salts are 28.7%. Therefore, those binary systems always have lower melting points compared to pure salts. Hence, addition of a new combined salt can decrease the bond strength of original system and lower melting point, as shown in the figure 19.

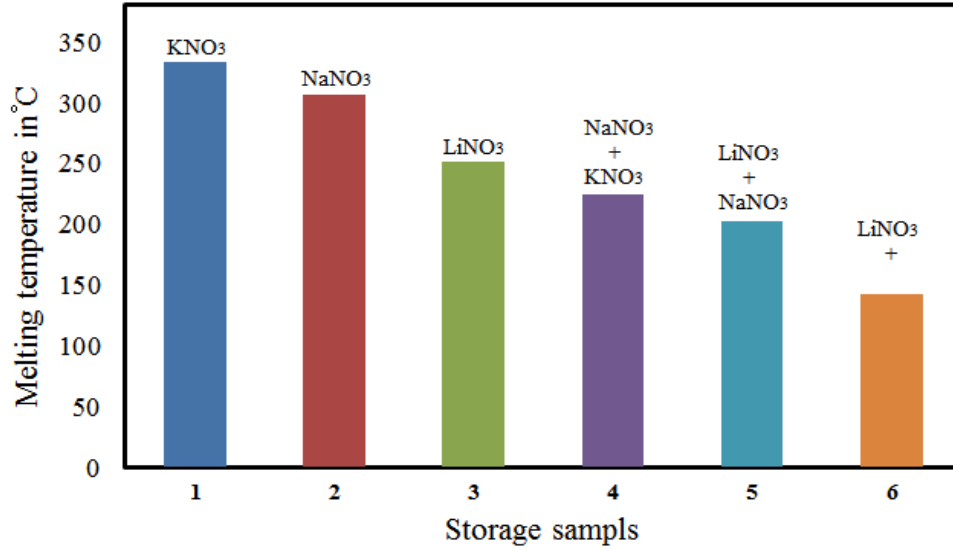


Figure 19. Melting point on pure and multi components of PCM

## 5.6 Charging time process comparison

Charging time in thermal storage process is the one parameter in order to absorb the solar energy during day time. As shown in the figure 20, it is possible to see that the total charging time of two samples is different. All the storages have by definition the same heating time for a 0.7 kW heating. It is noted that the temperature rises with time on the storage and expands inside the PCM; this phenomenon can be performed in terms of heat conduction and natural convection. According to charging time and liquid fraction of the NaNO<sub>3</sub>-KNO<sub>3</sub> material can cover the temperature much faster than the NaNO<sub>3</sub>-LiNO<sub>3</sub> at the same operating condition during the process. However, the liquid fraction times of NaNO<sub>3</sub>-KNO<sub>3</sub> material obviously 46% less than the NaNO<sub>3</sub>-LiNO<sub>3</sub> material. The total melting time reduces about 19.1% compared with the NaNO<sub>3</sub>-LiNO<sub>3</sub>. This indicates that the thermal energy storage performance of NaNO<sub>3</sub>-KNO<sub>3</sub> mixture of salt is better and the melting process is faster than the NaNO<sub>3</sub>-LiNO<sub>3</sub> mixture of salt under the same operating condition.

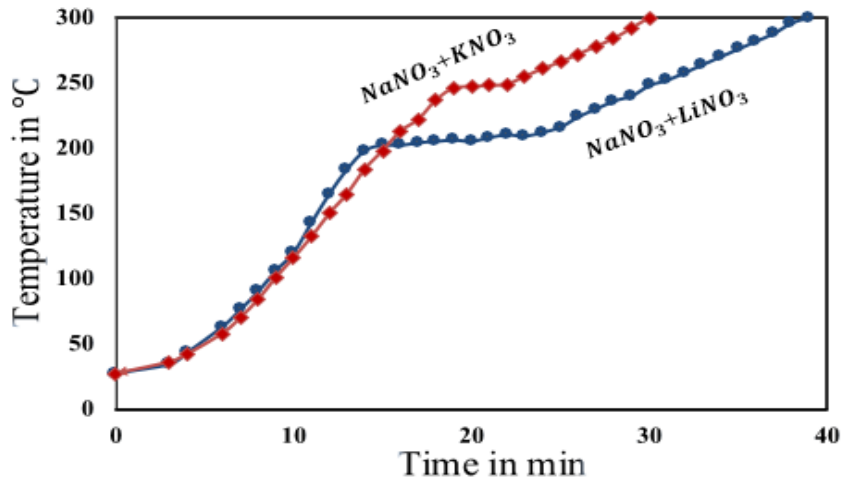


Figure 20. Temperature-Time curve during charging

### 5.7 Discharging time comparison

Variation of PCM temperatures Figure .18, represents the temperature histories of PCMs during discharging process. It is seen from the figure 21 that the two samples temperatures drop is large until the PCM reaches its phase transition temperature. due to the large variation of oil temperature and PCM temperature at the beginning of the discharging process. After that the temperature drop the PCM releases its latent heat. In the case of NaNO<sub>3</sub>-KNO<sub>3</sub> PCM material temperature is nearly constant for 11 min, but the NaNO<sub>3</sub>-LiNO<sub>3</sub> temperature is nearly constant for 25 min. After complete their solidification, their temperature starts decreasing until the PCM temperature reduces to be in order of 150°C, but the rate of temperature drop between two material are not equals. Generally, the total discharging time of NaNO<sub>3</sub>-KNO<sub>3</sub> about 6% reduces than NaNO<sub>3</sub>-LiNO<sub>3</sub>. This indicates that the thermal energy storage performance of NaNO<sub>3</sub>-LiNO<sub>3</sub> mixture of salt is better and the discharging process is slightly longer than the mixture of NaNO<sub>3</sub>-KNO<sub>3</sub> salt under the same operating condition.

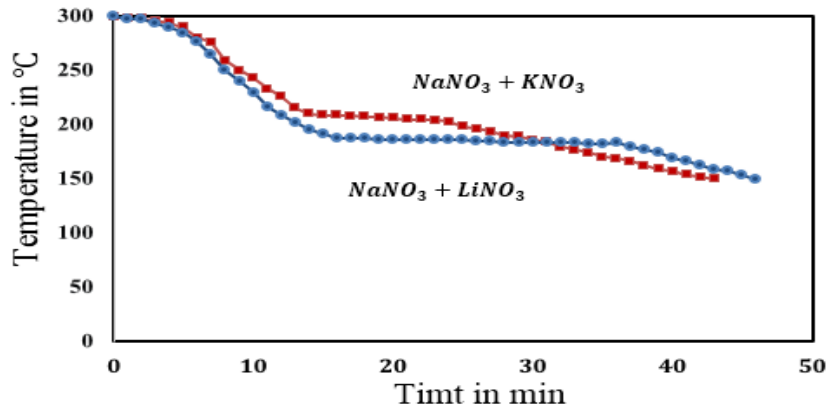


Figure 21. Temperature-Time curve during discharging

In the case of discharging and high latent heat the salt mixture of  $\text{NaNO}_3\text{-LiNO}_3$  would be a good candidate but Lithium nitrate increase its compound cost of salt at the same time the increases the charging time. The cost of salt mixture  $\text{NaNO}_3\text{-LiNO}_3$  increase more the cost of a two samples cost per storage performance would be much higher due to increase cost to the decrease storage performance.

### 5.8 Characterization of Storage Material

In this subsection is discussed the detailed description of experimental results of storage materials. The conducted results are the melting point, latent heat of fusion, specific heat capacity and the density on the mixture of sodium nitrate and potassium nitrate sample with different mass ratio, which is, to address the thermal potential of each mixtures and the effect of the mass percentage. Experimental result for each ratio plotted the temperature-time curve during melting process, as shown in Figure 22.

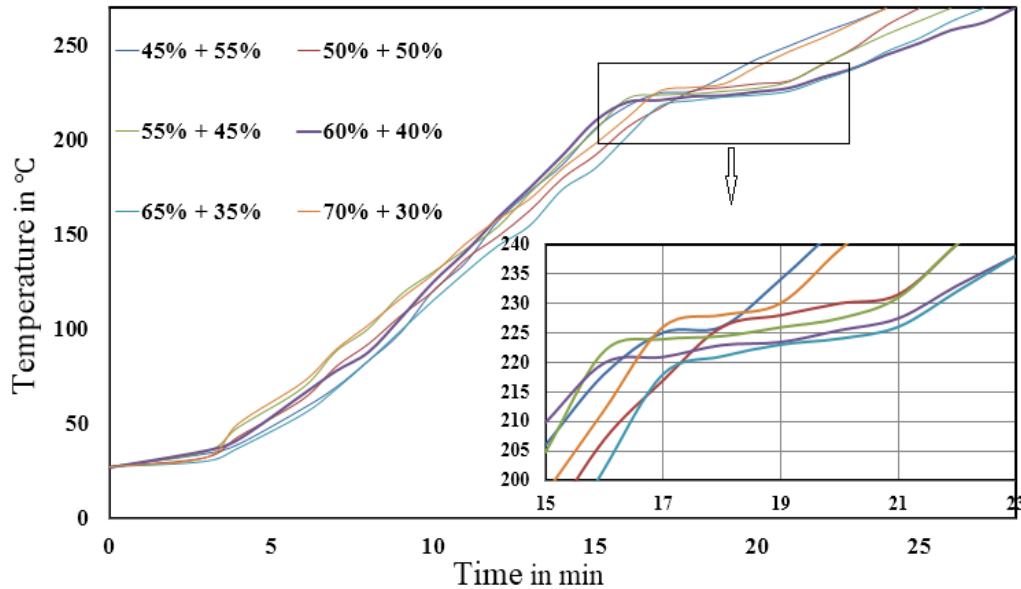


Figure 22. Temperature-time response of PCM mixture salts during melting process

The slopes of the temperature change during the sensible heat increases with time for the first 16 to 17 min and then become almost flat for different specific time. During this period, the solid to liquid melting process occurred in a specific temperature range.

Figure 5.7 shows temperature-time curve result of 45% - 55% sample mass ratios. The melting point is 223.5°C and maintained at this temperature for 1.5 min. This shows that the melting point is promising and is in the required range for potential cooking application. The heat absorbed per kilogram of the sample as a latent heat is 28.18 kJ/kg, and specific heat capacity at the solid state is around 1252 J/kg°C and above the melting point it increases with temperature. It is about 2537 J/kg°C in. the absorbed heat above the melting point becomes very high, duo to the specific heat at that point.

The plot is indicated that the melting point by 50% - 50% mass ratios sample is 228.5°C. The heat absorbed per kilogram of the sample as a latent heat is 56.34, kJ/kg for 3 minutes, and specific heat capacity at the solid state is around 1633 J/kg°C and above the melting point it increases with temperature. It is about 1909.8 J/kg°C in the liquid region. Here in this sample the melting point is promising and is in order of required range.

The melting point of the sample 55% - 45% mass ratio is 226 °C, the heat absorbed per kilogram of the sample as a latent heat is 98.14 kJ/kg, and for 4.8 min. and specific heat capacity of the sample in the solid region is around 1104 J/kg°C. The specific heat increases in the liquid region and it is around 2347 J/kg°C and it absorbs moderate amount of energy which makes it more preferable for storage application.

As indicated in the melting point of 60% - 40% sample mass ratio is 225. °C, the heat absorbed per kilogram of the sample as a latent heat is 101.4 kJ/kg, the latent heat maintained for 5.4 min. and the specific heat capacity of the sample in the solid region is around 1205 J/kg°C. The specific heat capacity was higher in the liquid region and it is around 3066 J/kg°C in this sample the melting point is promising and is in order of required range. It is absorbing large amount of energy in the latent heat reign, which makes it more preferable and highly promising for thermal energy storage.

That the melting point of the sample 65% : 35% mass ratio is 222°C, maintained this temperature for 4 min. the enthalpy of fusion as a latent heat is 75.12 J/kg, and specific heat capacity of the sample in the solid region is around 1268.9 J/kg°C. The specific heat increases with the temperature in the liquid region and it is around 2560.9 J/kg°C; Here in this sample the melting point is promising and is in order of required range. It absorbs moderate amount of energy which makes it more preferable

The melting point of the sample of 70% - 30% mass ratio is shows, that the melting point is promising and is in the required range for potential cooking application. The melting point is 228.4°C; maintaine this point for 1.2 min. enthalpy of fusion is 30.98kJ/kg and the specific heat capacity in the solid region seems uniform at about 1252J/kg°C. In the liquid region it is around 3380 J/kg°C.

Generally, all samples melting point is promising and is in the required range for potential cooking application. But having good melting point did not guarantee the use of this sample for utilization for the required application. The absorbed latent heat per a given mass of the sample and sensible heat absorbed after the melting point as the temperature increases should be considered. Therefore, the sample of (60% NaNO<sub>3</sub>-40% KNO<sub>3</sub>) by mass ratio it absorbs large amount of energy as the latent heat value and sensible heat absorbed after the melting

point, which makes it more preferable and highly promising for thermal energy storage. The absorbed energy per a given amount of sample should be in order of 101.4 kJ/kg and above for consideration as good thermal energy storage.

## 5.9 Enthalpy

The temperature-time curve is a key factor in describing the total thermal energy storage capacity of PCMs. The temperature-time curve provides information on the combined effect of latent heat and sensible heat. The study of enthalpy total energy storage (TES) is very crucial when eutectic mixtures are used to maintain the thermal performance. In general, eutectic mixtures in this case decrease the measured latent heat per unit mass due to the decrease of the active PCM in the overall mixture. The eutectic mixtures evaluated at various mass fractions. The optimum mass fraction effect of eutectic mixtures evaluated in order to found the maximum latent heat as can be seen in figure 21. However, totals energy storage of PCMs is a combination of latent heat and sensible heat. Therefore, an increase in specific heat capacity can partially compensate for the reduction in latent heat. The increase in the latent heat with the optimum mass fraction leads to an increase of contribution toward the total TES is very important.

The enthalpy TES at different mass ratio and specific heat for the solid state is calculated as the slope of the temperature-time curve before the phase transition region (sensible heat of solid state). Similarly, the specific heat capacity for the liquid state is calculated as the slope after the phase transition region (sensible heat of melted state). The (TES) over a temperature range of 270°C for various mass ratios of PCM mixtures, it can be observed in Fig 23.

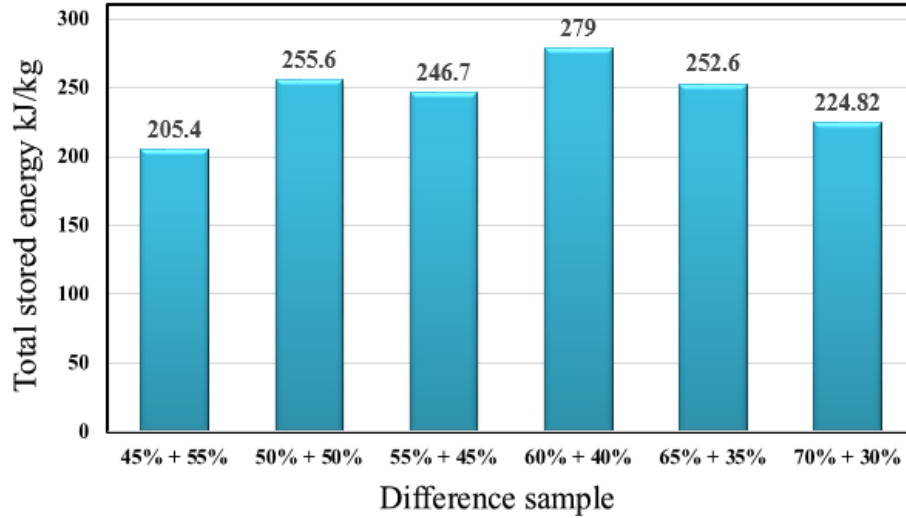


Figure 23. Effect of LHSS and mass fraction on the total thermal energy storage

### 5.10 Discharging process

In this discharging process result conducted in the case of with load and without load application discussed. As shown in the figure 24 represents the temperature curve of PCM and oil are changing with time during discharging process. It is seen from the figure that the PCM temperature drop is large until the PCM reaches its phase transition temperature, due to the large variation of oil temperature and PCM temperature at the beginning of the discharging process. As the same time the oil starts to absorb the heat rapidly. After that the PCM temperature drops, the PCM releases its latent heat for a long duration. In the case of continuous discharging process, the PCM temperature is nearly constant for 11 min. After complete solidification of the PCM, its temperature starts decreasing until the PCM temperature reduces to be in order of 150°C, however, the rate of temperature drop is not as high as in the beginning of the discharging process. This is due to low temperature difference between the PCM and load temperature though the solid PCM releases its sensible heat. Then the oil starts to decline with time because of the change in the thermal resistance of the solidified layer of the PCM.

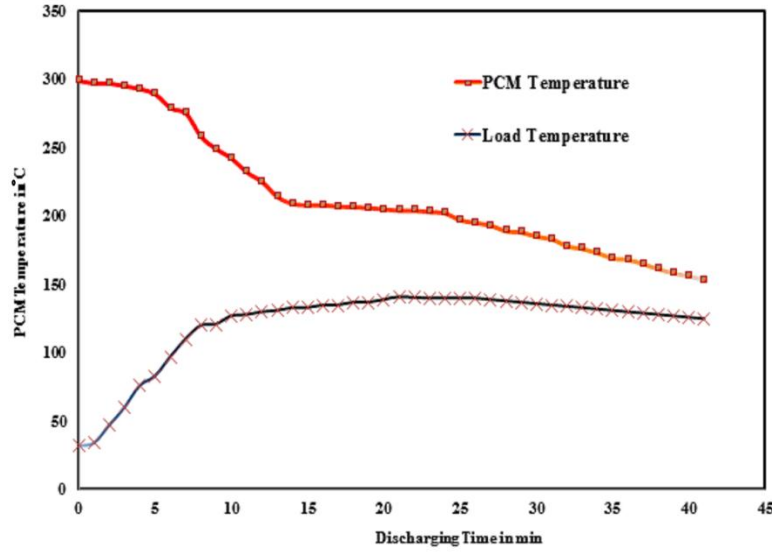


Figure 24. Discharging process with time

### 5.11 Density

The selected PCMs density was measured and summarized in Table 12. The density of PCM at the solid phase about 27°C below the experimental melting temperature and for the liquid phase at about 300°C above the experimental melting temperature was measured and during this phase transformation a desirable small volume expansion was observed.

Table 12. Density determination of salt mixture of NaNO<sub>3</sub>: KNO<sub>3</sub>

| materials                               | $V_{initial}$ in cm <sup>3</sup> | $\Delta V$ in cm <sup>3</sup> | $\beta$ | $\rho_{solid}$<br>kg/m <sup>3</sup> | $\rho_{liquid}$<br>kg/m <sup>3</sup> |
|-----------------------------------------|----------------------------------|-------------------------------|---------|-------------------------------------|--------------------------------------|
| (NaNO <sub>3</sub> : KNO <sub>3</sub> ) | 928.5                            | 123                           | 0.00048 | 2154                                | 1901                                 |

It was noted that the selected PCMs which belong to the inorganic molten salt mixture PCMs have an acceptable decrease in their density but increase their volume when they melt. Therefore, their volume expansion during phase transformation from solid to liquid are minimal and not expected to cause any problems in storage tank for any applications. For that reason, these kinds of PCMs are considered to be very attractive for TES applications, because the required empty space that is equivalent to 14% and their volume expansions is very small within this temperature range.

## CHAPTER SIX

### 6 CONCLUSION AND RECOMMENDATION

#### 6.1 conclusion

Three predominant heat storage materials were picked based on the literature survey for this study, namely sodium nitrate, potassium nitrate and Lithium nitrate to evaluate their thermal performance. Theoretical and experimental investigations were conducted by taking different mass ratios of PCM samples. Following are the below conclusions:

A 60% of  $\text{NaNO}_3$  and 40% of  $\text{KNO}_3$  mass ratio eutectic binary mixture was found to be the most promising PCM for household cooking applications, because of its suitable phase transition temperature and high latent heat of fusion.

From experimentation it was found that the 60% of  $\text{NaNO}_3$  and 40% of  $\text{KNO}_3$  mass ratio has the thermal characteristics of single melting phase change temperature of  $225^\circ\text{C}$ , the latent heat of fusion  $101.4 \text{ kJ/kg}$  and total TES capacity was  $279.2 \text{ kJ/kg}$ . In addition to other thermo-physical properties such as specific heat capacity, thermal conductivity, and density, were experimentally determined.

From experimentation it was found that the potential heat energy available in the best sample for potential cooking is  $253.9 \text{ kJ/kg}$ . The Energy required to cook lunch and dinner for six members in an urban family is  $2200.7 \text{ kJ}$ . Therefore, to store  $2200.7 \text{ kJ}$  of energy  $8.7 \text{ kg}$  of PCM or  $4.58 \text{ liters}$  of PCM is needed.

Therefore, the PCM ' $\text{NaNO}_3 + \text{KNO}_3$ ' by mass ratio of 60% to 40% is the most promising eutectic mixture because of its characteristics like low charging time, high discharging time, and small tank for storing at home. It can be very well recommended for cooking applications in both the rural and urban areas.

## 6.2 Recommendation

- Even though different parameters are investigated and analyzed during the study still there are other remaining works to be investigated by different scholars in the area. The observations for further investigation are summarized as follows.
- Since solar energy is the most available and promising source of thermal energy, it is recommended to design a storage system which can efficiently tap this solar energy for future use.
- Most industries in Ethiopia are energy huggers, a great chunk of their energy is lost to the environment during the working process. Hence, the designed storage system of this study i.e. a eutectic mixture of  $\text{NaNO}_3 + \text{KNO}_3$  (60 + 40% m/m) can be effectively used as a heat recovery system.

## 6.3 Future work

Based on the attained main conclusions, the forthcoming research activities will be focused on research lines: The second research line targets the evolution of the LHTES design and manufacturing procedure to increase the economic competitiveness of the actual LHTES system.

The  $\text{NaNO}_3 + \text{KNO}_3$  eutectic mixtures investigated showed potential as a PCM for the cooking application. However, since a slight density difference between two components further research is required to evaluate the thermal stability of the eutectic mixtures for long periods of use under conditions representative of actual applications.

Thermal chemical incompatibility and density will be also performed in the future to complete the PCMs' evaluation.

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