Eutectic Composition of Selected Phase Change Materials for Thermal Energy Storage Applications

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Abstract- Latent heat storage in salt mixture has drawn so much attention because of the salt mixture’s capability of storing large quantity of heat when compared to single salt thereby, making it more feasible for use as phase change material. However, it is worthwhile to find out among various combination of salts forming eutectic mixtures, the one that has the best energy storage capability by evaluating and comparing their melting points and latent heat storage. So, in this research work, four different types of eutectic mixture of salts were prepared and experimentally investigated for the best thermal energy storage capability. The first eutectic mixture consists of 2.6g of LiNO₂, 6.4g of NaNO₂, 1g of NaNO₃ and 1g of Na₂CO₃. The second eutectic mixture consists of 1.75g of LiNO₂, 3.9g of NH₄NO₃ and 1.9g of KNO₃. The third one consists of 5.2g of LiNO₂, 13.7g of NaNO₂ and 1g of NH₄Cl and the fourth one consists of 1.77g of LiNO₂, 2.94g of NH₄NO₃, 1g of NaNO₃ and 1g of NaCl. The latent heat and the melting point of the respective salt and their eutectic mixture were determined using digital differential scanning Apparatus. The results obtained showed that the melting points and latent heats of the first, second, third and fourth eutectic mixture were 79.5°C and 112kJ/kg, 80.5°C and 114kJ/kg, 81.4°C and 109kJ/kg, 84.4°C and 119kJ/kg respectively. In view of this, the eutectic mixture of 1.77g of LiNO₂, 2.94g of NH₄NO₃, 1g of NaNO₃ and 1g of NaCl with melting point of 84.4°C and latent heat of 119kJ/Kg was found to possess the best thermal energy storage capability compared to others.

Keywords- Eutectic mixture, Salts, Phase change materials (PCM), Latent heat storage

1 INTRODUCTION

Energy storage and supply is an area of research that can be looked back on a relatively long tradition, as the basic concepts were discovered back at the end of the nineteenth century. The increasing liberalization and globalization of the energy markets not only creates new overall conditions but places new demands on the energy supply systems for the future (Cao et al., 2015). However, there are limitations in energy storage which means that not much has happened, apart from that seen a few years ago with regard to storage density of hydrogen possible on carbon nanotubes (Sabur, 2018). This observation, however, conceals a host of developmental steps, some of them using effects on nanoscale, which have led to significant progress in energy storage facilities in the past few years (Julien et al., 2013). The reasons for thermal energy storage are many; for example, electrochemical batteries provide an excellent portable source of electricity. A typical gas generator uses stored heat of combustion in gasoline to provide portable and reliable electricity in cases of power failure.

These energy storage types are only a few examples of a huge array of the technologies in use today (Prakah et al., 2008). Thermal storage system is predominantly used where there exist a mismatch between electricity production and use of renewable energies which are by nature intermittent and its availability is decreased through weather perturbation. Solar energy requires efficient thermal power storage so that the excess heat collected all through sunshine hours can be saved for during the night (Farid, et al., 2004). Similar problems occur in heat recovery systems and industrial processes where the waste heat availability and utilization periods are different, requiring some thermal energy storage.

Also, electrical power consumption varies extensively all through the day and night, especially in extremely cold and hot climate countries. Where the major phase of the variant is due to domestic house heating and air conditioning. Such variation leads to an off-peak period, generally after midnight till early morning (Farid, et al., 2004). Accordingly, electricity stations must be designed for capacities enough to fulfil the high load. Better energy management can be achieved if some of the peak load is desired to be shifted to the off-peak load period using energy storage system. Hence, the successful utility of load shifting relies largely on the approach of energy storage adopted (Ricerca, 2015).

Generally, it is viable to divide thermal storage structures into active and passive systems. An energetic storage device consists of a mechanically assisted component for enabling heat transfer between machine and heat source. This device is composed of a convection heat switch fitted into the storage cloth that circulates through a heat exchanger, a photo voltaic receiver or a steam generator. In a passive storage system, the heat switch between the system and the heat supply through natural convection or buoyancy forces (due to density gradient) without the help of any external units (Kuboth, et al., 2017). Active storage structures can be divided into direct and indirect systems. In the direct systems, the heat switch fluid (HTF) is use as a storage medium, whilst in the indirect systems; a second medium is used for storing the heat (Furbo, et al., 2008). Salt hydrates are the most energy intensive of the PCM possibilities for energy storage. So, in selecting a PCM for an application, the operating temperature of the heating or cooling should be matched to the transition temperature of the PCM.

Phase change materials (PCM) on the other hand are “Latent” heat storage materials. The thermal energy transfer occurs when a material changes from solid to liquid, or liquid to solid. This is called a change in state,
or “Phase.” Initially, these solid-liquid PCMs perform like conventional storage materials; their temperature rises as they absorb heat. Unlike conventional (sensible) storage materials, PCM absorbs and release the absorbed heat at a nearly constant temperature. They store 5-14 times more heat per unit volume than sensible storage materials such as water, masonry, or rock.

Many PCMs are known to melt with a heat of fusion in any required range. However, for their employment as latent heat storage materials they should exhibit some certain desirable thermodynamic, kinetic, and chemical properties. Moreover, economic considerations and easy availability of these materials has to be kept in mind (Lin et al., 2012). The PCM used in the design of thermal-storage systems passes the desirable thermo-physical, kinetics and chemical properties. (Pop, et al., 2017) and (Nussbaumer, et al., 2006). The storage of thermal energy depends heavily on the medium on which it is stored. To fully utilize the latent heat release during melting (discharge period), a PCM must meet both the desired melting point and latent heat requirements of the system. For example, a solar collector charging a hot water latent TES system would not use water/ice as the PCM, since water is already in the liquid state at room temperature. Likewise, one could not use heavy metals such as copper or iron as a PCM, since the melting temperature is much too high, and would not be reachable in a solar collector. It is for this reason that a great number of PCM materials have been studied in the literature and a detailed review of over 250 PCMs and their characteristics can be found in (Sharma, et al., 2009).

A lot of work has been done on the use of PCM as thermal energy storage material and notably, Rabin et al., (1995) developed a mathematical and experimental model for the charging method of a reflector storage system integrated with salt hydrate as a PCM. The researchers used the enthalpy-based finite distinction methodology and unheeded the impact of convection. The projected model showed high correct validation with the experimental PCM temperature measurements. However, the neglect of the convection heats transferred within the PCM reduced the accuracy of their mathematical predictions. Mettawee and Assassa (2006) created a compact reflector consisting of an absorbent instrumentation 1.3 m long and leaning 45°. The instrumentation was stuffed with paraffin with melting temperature of 53.5°C and a copper pipe with 0.012m diameter and 1.35m length was immersed into it. The charging results showed that the temperature of the PCM redoubled at a coffee gradient because of the low thermal physical phenomenon of the solid PCM. Once the PCM melted, the temperature difference between layers decreased due to the natural convection effect. The discharging results showed that the discharge mass flow and the natural heat transfer constant had a good influence on the reflector performance.

Eames and Griffiths (2006) developed a transient finite volume model to research the thermal behaviour of an oblong reflector stuffed with water and different concentrations of the PCM suspension. The PCM suspension had a melting temperature of 600°C. The developed model was used to calculate the temperature profile. The energy augmentation simulation of the identical experiment showed that water was more practical in storing energy for a protracted material. This was due to the lower convective heat loss coefficients within the PCM and its higher temperatures that redoubled the heat loss from the PCM suspension. The authors found that integrating the PCM suspension in the solar collector leads to a marginal reduction in the collector efficiency. Saw and Al-Kayiem (2011) presented an experimental investigation on the thermal performance of a flat-plate collector with PCM. The experiment ran for a full day, under varied water mass flow rate, that is, 4, 8, and 10 kg/min, and varied flat plate collector’s tilt angles of 0°, 10°, and 20°. The results revealed that optimum hot water temperature of 66°C was obtained when the tilt angle was 0° and the mass flowrate of water was 4kg/min.

Lin et al, (2012) projected a comparative experimental study, underneath a typical sunny day in Asian nation, to research the chance of enhancing the performance of a flat-plate reflector by group action paraffin with a melting temperature of 60.45°C directly in reality with the collector absorbent plate. The projected system was studied and compared with the standard collector at 3 completely different inclination angles together with 10°, 20°, and 30° and constant water mass flow of 0.5 kg/min. The results showed that the combination of PCM redoubled the thermal absorption to 71.15% and reduced the thermal heat losses to below 4.34 W/m2K. Naghavi et al, (2014) research work was analytically aimed at controlling the overheating issue of the supplied water during the day and also to extend the operation time of the solar water heater. The model consisted of a heat pipe flat-plate collector system with the addition of paraffin with a melting temperature of 64°C to store energy. The system was studied using 20, 40, 60, and 80 heat pipes with a block thickness of fifty metric linear units and water mass flow of 0.05 kg /s. The results of the experiment showed that the absorbed radiation was roughly sixthieth of the recorded solar radiation.

Naghavi et al, (2015) proposed a theoretical model based on a one phase Stefan problem to investigate the thermal performance of integrating PCM to the manifold of an evacuated tube heat pipe solar collector system. It was evident that the usable light volume and thermal efficiency of the baseline system considerably decrease with the increment within the water volume. The usable volume and the thermal efficiency almost remain the same in the innovative system. This shows the flexibility of projected system to produce energy with independence on the operation conditions because of the keep energy within the PCM. Although a reasonable work has been done on thermal energy or latent heat storage in PCM, the need to device a means of obtaining optimum performance of this system cannot be overemphasized. Latent heat storage in salt mixture has drawn so much attention because of the salt mixture’s capability of storing large quantity of heat when compared to single salt thereby, making it more feasible for use as phase change material. However, it is worthwhile to find out among various combination of salts forming eutectic...
mixtures, the one that has the best energy storage capability by evaluating and comparing their melting points and latent heat storage. Therefore, the aim of this work is to produce four different types of eutectic salt mixture and evaluate their thermal energy storage capabilities with a view to finding the best among them.

2 MATERIALS AND METHOD
The following salts shown in Plates 1, 2, 3, 4, 5 and 6 with the following properties were used to carry out this work: Lithium Nitrate (LiNO₃), Molar mass: 68.946 g/mole, melting point: 255°C. Boiling point: 600°C, Density: 2.38 g/cm³ Ammonium Nitrate (NH₄NO₃), Molar mass: 80.043 g/m, melting point: 169.6 °C, Boiling point: 210 °C Sodium Nitrate (NaNO₃), Molar mass: 84.9947 g/mole, Heat capacity (C): 93.05 J/(mol K), Melting point: 306 °C Potassium Nitrate (KNO₃), Molar mass: 101.1032 g/mole, Melting point: 338°C, Boiling point: 400°C, Density: 2.109 g/cm³ Ammonium Chloride (NH₄Cl), Molar mass: 53.491 g/mole, Melting point: 338°C, Boiling point: 520°C Sodium Chloride (NaCl) Molar mass: 58.44 g/mole, Melting point: 801°C. Boiling point: 1413°C.

2.1 PRODUCTION OF PCM
There are various metallic salts with different properties that can be used as a phase change material. In this research work six (6) different salts were critically analysed using standard apparatus. The salts included (i) Sodium nitrate (ii) Ammonium chloride (iii) Potassium nitrate (iv) Lithium nitrate (v) Sodium chloride and (vi) Ammonium nitrate. Each salt was separately analysed using the method below. The experiments were done four different times more so, with salts combined. Four different 250 ml PYREX® Griffin beaker as shown in plate 7 and spatula were washed with distilled water and oven dried in a Genlab incubator as shown in Plate 8.

The percentage by weight of the samples was measured using the Mettler AT 400 machine as shown in plate 9. The first (experimental procedure) consists of 2.6g LiNO₃ +6.4g NH₄NO₃ + 1g NaNO₃ were all combined and thoroughly mixed together in a 250 ml PYREX® Griffin beaker and sealed at the top to prevent salt escape by evaporation. The same was done for experiment 2, (1.75g LiNO₃ +3.9g NH₄NO₃ +1.1g KNO₃) experiment 3, (5.2g LiNO₃ +13.7g NH₄NO₃ +1g NH₄Cl) and experiment 4 (1.77g LiNO₃ + 2.94g NH₄NO₃ +1g NaNO₃ +1g NaCl) respectively. What motivated the mass of the identified salts are the specific capacities of the samples used in the investigation. The respective samples were then heated in...
the furnace above their melting point to obtain the molten sample. After the first experimental procedure was completed, the samples in each beaker was pound using a laboratory mortar and pestle, as shown in Plate 10 (the fined grained obtained was then poured in a separate beaker tagged sample 1.

The same process was followed with the other respective salts. After thorough salt mixture, a fraction of each of the sample was tested for solubility. It was discovered that the mixture was not completely soluble in water as seen by visual examination. 50ml of ethanol was then used for the solubility check as shown in plate 11. Eventually all the samples dissolved in ethanol as also seen by visual examination. Another 50ml of oil paint as shown in plate 12 was then measured and mixed with the dissolved salt to see if there will be separation or not.

It was discovered that the mixture blended well. The salt mixture was put in four different melting point capillary strips as shown in Plate 13 compacted together and inserted in a Griffin melting apparatus as shown in Plate 14 to check for its melting point.

The readings were recorded at the point when the mixture begins to dissociate from each other. The point of initial dissociation is known as the upper bound and the points where all the salts becomes liquid is the lower bound. The latent heat capacity of the individual salt and that of individual eutectic salt mixture were measured with a digital differential scanning apparatus (DDSA). This was done by introducing the weighed samples of the salt and eutectic mixture individually into the DDSA and operated at heating rates of 100C/min and 200C/min and with a temperature range of 45-1200C at constant atmospheric pressure. So, the latent heat of the individual salt and eutectic mixture were recorded. The experiments were carried out in Federal University of Technology Minna, Nigeria.

### 3 RESULTS AND DISCUSSION

The results of the formulation of the PCM are shown in Tables 1-3. Tables 1 and 2 are organic materials standalone PCM which are flammable in nature and should not be exposed to extreme high temperature, flames or oxidizing agents because these organic materials possess features such as high heat of fusion, inflammability, low thermal conductivity, low flash points, varying level of toxicity, and instability at high temperatures.

| Sample No. | Material | Melting Temperature (°C) | Melting Enthalpy (KJ/kg) |
|------------|----------|--------------------------|--------------------------|
| 1          | Xylitol C₆H₁₂(OH)₆  | 94                        | 263                      |
| 2          | D-Sorbitol C₆H₁₀(OH)₆ | 97                        | 185                      |
| 3          | Erythritol C₆H₁₂(OH)₆ | 120                       | 340                      |
| 4          | D-Mannitol C₆H₁₄(OH)₆ | 167                       | 316                      |
| 5          | Galactitol C₆H₁₂(OH) | 188                       | 351                      |

| Sample No. | Material | Melting Temperature (°C) | Melting Enthalpy (KJ/kg) |
|------------|----------|--------------------------|--------------------------|
| 1          | LiNO₂ | 254                       | 360                      |
| 2          | NaNO₂ | 307                       | 172                      |
| 3          | KNO₃ | 333                       | 266                      |
| 4          | MgCl₂ | 714                       | 452                      |
| 5          | NaCl | 800                       | 492                      |
| 6          | Na₂CO₃ | 854                       | 276                      |
| 7          | KF | 857                       | 452                      |
| 8          | K₂CO₃ | 897                       | 236                      |
Table 3 shows the eutectic composition of different salt with different properties reacting together to achieve a property which differs from individual salt when considered with Table 2. The melting point and latent heat of the first, two samples in Table 3 progresses progressively, while the third sample has a latent heat of 109kJ/kg and a melting point of 81.4°C. Latent heat in this case is the amount of heat required to bring about a change of state in a substance, and the substance been referred to here is the eutectic mixtures samples detailed in Table 1. The mixture of salt water and air contains heat and part of this heat is represented by sensible temperature which is measured by the aid of a thermometer while the latent heat is the energy that was used to evaporate the moisture in the salt that the air contains. If the air contains a great deal of water vapour, its latent heat will be high. The last sample which consists of four different salts with melting point of 84.8°C and latent heat of 119kJ/kg as shown in Table 3, has the best thermal or latent heat storage potentials because its latent heat supersedes that of others and the most importantly its melting point which is lower compared to Table 1-2. The melting phase is termed important because it is a physical process that results in the phase transition of the eutectic mixture of the salts from solid to liquid. The longer it takes for this eutectic mixture to dissolve the better its phase change properties. The sum of the sensible and latent heat of the air in each of the respective samples is referred to as “enthalpy” sometimes called “total heat”.

### 4 Conclusion

Salt based phase change materials are used in many applications for thermal energy storage. Continuous improvements are required to meet up with the requirements of the vast number of their applications. Considering this, four different types of eutectic salt mixtures were produced, and their melting points and thermal energy storage capabilities were evaluated and compared. The quaternary eutectic salt mixture (LiNO₃+NH₄NO₃+NaNO₂+NaCl) with melting point of 84.4°C and latent heat of 119kJ/kg has the best thermal energy storage capability by virtue of its possession of the highest amount of latent heat compared to others. Out of the ternary eutectic salt mixtures (LiNO₃ + NH₄NO₃ + NaNO₂, LiNO₃ + NH₄NO₃ + KNO₃ and LiNO₃ + NH₄NO₃ + NH₄Cl), ternary eutectic salt mixture (LiNO₃+NH₄NO₃+KNO₃) with melting point of 80.5°C and latent heat of 114kJ/kg was found to possess the best thermal energy storage capability. It can be concluded based on the results obtained in this research work that the higher the number of salts combined to produce eutectic salt mixture, the better the thermal energy storage capability.

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