SYNTHESIS OF MOLTEN SALT AS HEAT TRANSFER FLUID FOR WASTE HEAT RECOVERY APPLICATION

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ABSTRACT

Basically, various materials such as water, oil heat, ionic liquids and also molten salt are selected to serve as heat transfer fluid. The properties of the different heat transfer fluid determine their performance in any application. The development of nitrate molten salt with different constituent salt are studied to characterize the physical and thermal properties based on low melting point and high thermal stability in order to be considered as heat transfer fluid in waste heat recovery applications. The nitrate based molten salt that has been use in this study consists of binary, ternary and quaternary salt mixture with different weight composition. Molten salt mixture has been dried in the furnace for 12 hours before mixing. After mixing, the salt mixture was heated in furnace at 150 ºC for 4 hours and increased the temperature to 400 ºC for 8 hours for homogenize the salt mixture. The temperature was reduced to 115 ºC for 1 hour before removed from furnace. Thermal analyses were performed using differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). These analyses were conducted to obtain the melting point, thermal stability and heat capacity of molten salt and fulfill the targeted characteristic of a heat transfer fluid. The result shows the melting point for ternary and quaternary mixtures are closely 100 ºC where the value is 92.4 ºC and 98.9 ºC compared than binary mixtures. Thermal stability analyzed in this study shows that the value for all mixture above 500 ºC but quaternary mixture showed the highest thermal stability which the value is 701 ºC. For heat capacity value of all mixture shows a range between 2.5 – 4.7 J/g ºC and quaternary mixture showed the highest value of heat capacity when compared to all mixture with value of 4.7 J/g ºC. For the conclusion, the quaternary salt mixture has fulfilled the targeted characteristic as heat transfer fluid with low melting point, high thermal stability and heat capacity.

ABSTRAK

Pelbagai bahan telah dipilih untuk bertindak sebagai cecair pemindahan haba seperti air, minyak, cecair ionik dan juga garam lebur. Perbezaan pada ciri –ciri bahan tersebut yang menentukan prestasi bahan dalam sebarang aplikasi. Pembangunan garam lebur berasaskan nitrat dengan konstituen yang berbeza dikaji untuk mencirikan sifat fizikal dan termal bagi mendapatkan takat lebur yang rendah serta kestabilan termal yang tinggi untuk dipertimbangkan sebagai cecair pemindahan haba sebagai aplikasi sisa pemulihan haba. Garam lebur berasaskan nitrat yang digunakan terdiri daripada campuran garam binari, ternari dan quaternari dengan komposisi yang berbeza. Campuran garam lebur akan dikeringkan di dalam relau selama 12 jam sebelum proses campuran berlaku. Selepas pencampuran, garam akan dipanaskan dalam relau pada suhu 150 ºC selama 4 jam dan dinaikkan pada 400 ºC selama 8 jam bagi menyeragamkan campuran. Suhu akan dikurangkan pada 115 ºC selama satu jam sebelum dikeluarkan dari relau. Analisis terma yang telah dijalankan adalah *differential thermal analysis* (DTA), *thermogravimetric analysis* (TGA) dan *differential scanning calorimetry* (DSC) bagi mendapatkan nilai takat lebur, kestabilan terma dan kapasiti haba. Keputusan menunjukkan takat lebur bagi campuran ternari dan quaternari menghampiri 100 ºC dengan nilai 92.4 ºC dan 98.9 ºC berbanding dengan campuran binari. Analisis kestabilan terma menunjukkan nilai bagi semua campuran melebihi 500 ºC namun campuran quaternari mempunyai nilai kestabilan termal yang paling tinggi iaitu 701 ºC. Untuk nilai kapasiti haba pula semua campuran menunujukkan julat nilai antara 2.5 – 4.7 J/g ºC dan campuran quartenari adalah yang paling tinggi. Campuaran quaternari telah memenuhi ciri cecair pemindahan haba dengan takatlebur yang rendah, kestabilan termal dan kapasiti haba yang tinggi.

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LIST OF SYMBOLS

°C	-	Celcius
%	-	Percent
$NaNO_3$	-	Sodium Nitrate
$NaNO_2$	-	Sodium Nitrite
KNO_3	-	Potassium Nitrate
$Ca(NO_3)_2$	-	Calcium Nitrate
$LiNO_3$	-	Lithium Nitrate
HTF	-	Heat Transfer Fluid
TES	-	Thermal Energy Storage
STP	-	Standard Temperature and Pressure

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CHAPTER 1

Introduction

1.1 Background of study

Renewable energy sources such as wind, solar, water power, geothermal and biomass are playing more and more significant role in our energy supply. It is because the cheap cost and infinite amount of energy storage inside the resources. Besides that, solar energy is emphasized since 20^{th} century and viewed as promising alternative method to satisfy the large energy consumption every day in the world. Various materials are selected to serve as energy heating fluid such as water, oil heat, ionic liquids and molten salt. The properties of the different heat transfer fluid determine the performance of solar energy systems. Considering various physical and chemical characteristics relative heat energy storage system, molten salt has been proposed as a group that is suitable for a wide range of application temperature. They are emphasized in the application of solar energy because of a low melting point and high upper limit which can increase the stable working range.

Molten salt is defined as salt that is in solid state at standard temperature and pressure, (STP) but due to high temperature molten salt categorized as a liquid phase. The molten salt is usually in liquid form even at STP and is also known as ionic liquids. This molten salt has a variety of uses depending on the application used. Molten salts have been used in many industries as a high temperature heat transfer medium. For this research it is more focused to the molten salts that can be used as heat transfer fluid as well as for heat recovery system. Before molten salt was selected as the best, various solvents have been used as experimental materials including water, air, oil and sodium. Molten salt is used because it is a liquid at atmospheric pressure, non-flammable, low cost and efficient in store energy

(Jagadees, 2011). This paper describe the heat transfer fluid (HTF) consisting of a mixture of inorganic salts for use in concentrating energy applications. Previous commercially available molten salt heat transfer fluids have a high melting point, typically 140^{o}C or higher which limits their commercial use due to the risk of freezing (Suite, 2010). From previous studies have also found molten salt as heat transfer fluid by exploiting behavior eutectic composition novel materials, has led to low melting point of 65 °C and the thermal stability limit over 500 °C. There are various types of salt are now available in large commercial quantities from several suppliers. There are several formulations commercially available salt, mixed with nitrate or nitrite sold under various brand. The molten salt component are always used based on nitrate are sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), potassium nitrate (KNO_3), calcium nitrate ($Ca(NO_3)_2$)-tetrahydrated and lithium nitrate ($LiNO_3$).

Because of energy crisis nowadays, the utilization of low temperature waste heat draws more and more attention (Chen K *et al.*, 2014). The low temperature waste heat from solar thermal, geothermal, biomass, industrial and automobile, are among the potentially promising energy resources that capable to meet todays world energy demand (Salim, and Rafiq, 2012). Waste heat recovery through the application of Rankine cycle system is considered as an effective method of recovering the waste heat, as it aims to minimize the amount of heat wasted by the way of reusing it in either the same or a different process to produce a useful energy. Therefore, in this study, an alternative HTF based on inorganic salt will be introduced into the system in order to overcome the weakness of present molten salt HTF to applied in waste energy recovery. It is expected that the HTF exhibits both positive characteristics of HTF for example, lower melting point and high thermal stability.

1.2 Problem Statement

The lack of capability of heat transfer inside the cycle (evaporator) has led to ineffective operation of the cycle with generally small amount of recovered waste heat absorbed, and thus, small energy density is being generated by the system. Conventional approach to enhance the heat transfer by increasing the evaporator size will increase the system cost. Alternatively, improving the heat transfer process by mean of using an appropriate heat transfer fluid based on molten salt is considered as effective with low cost. Using a molten salt as a heat transfer fluid also can deliver significant advantages over alternatives such as mineral oil. The performance of molten salt much higher compared than other organic oil. It can handle temperatures up to 550ºC (Chhabara, 2010). However, from the previous study, HTF based on the molten salt have a high melting point typically up 240 ºC and expensive and the main problem is the molten salts freeze at relatively high temperatures in the range of 120ºC to 220ºC (Chhabara, 2010). A lower melting point in range of 60 - 120 ºC and a high thermal stability above 500 ºC are desired. Because such a fluid would enhance the overall efficiency of the plants by utilizing less energy to keep salt in the liquid state and by producing superheated steam at higher temperatures in the Rankine cycle. Because of this restraint, the alternative heat transfer fluid will be introduced to overcome the HTF nowadays with used mixture inorganic salt based on nitrate.

1.3 Objective

Objective of this research is:-

- To prepare nitrates based molten salt compositions with different constituent salts.
- To characterize the physical and thermal properties of molten salt based on various salt compositions
- To determine best composition molten salt based nitrate which achieved a lower melting point and high thermal stability of heat transfer fluid.

1.4 Scope

This investigation will conducted to synthesis of molten salt as heat transfer fluid for waste heat recovery application are:-

- The mixture of molten salt based on nitrate salt.

- Binary, ternary and quaternary eutectic mixtures of these salts have been proposed for the lower melting point and high thermal stability of the heat transfer fluid,
- The binary salt mixture studied in this work are 46 wt% Sodium Nitrate ($NaNO_3$), 54 wt% Potassium Nitrate (KNO_3) and 45.8 wt% Lithium Nitrate ($LiNO_3$), 54.2 wt% Potassium Nitrate (KNO_3).
- For ternary salt mixture studied in this work are 56.4 wt% Potassium Nitrate (KNO_3), 24.1 wt% Sodium Nitrite ($NaNO_2$), 19.6 wt% Lithium Nitrate ($LiNO_3$) and 67.2 wt% Potassium Nitrate (KNO_3), 19.3 wt% Calcium Nitrate ($Ca(NO_3)_2$, 13.5 wt% Lithium Nitrate ($LiNO_3$).
- For quaternary salt mixture studied in this work are 40wt% Potassium Nitrate (KNO_3), 15wt% Sodium Nitrite ($NaNO_3$), 20wt% Lithium Nitrate ($LiNO_3$), 25wt% Calcium Nitrate ($Ca(NO_3)_2$
- Characterization physical and thermal properties using some of analysis testing such as thermo gravimetric analysis (TGA) for the thermal stability, differential scanning calorimetry (DSC) will be observed the heat capacity and. Differential Thermal Analysis (DTA) will be measured the melting point.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

For concentrated waste heat recovery system, the type of liquid heat carrier has a direct effect on this system. Using heat transfer fluid, electricity can be generated even when sunlight is not available. Some organic materials such as oil and inorganic materials such as molten salts have been proposed for use as a heat transfer fluid potential. Lack of capacity of the heat transfer in the cycle has led to the ineffectiveness of the operation cycle with a small amount of waste heat generally reabsorbed, and with it, a small energy density is generated by the system. For this reason the material used as the heat transfer fluid requires improvement in thermal stability associated with material properties (Villada *et al.*, 2014). By using organic liquid it cannot reach temperatures above 400ºC with acceptable performance, because degradation into components that cannot be used at high temperatures. At temperatures above 400ºC, the liquid becomes inoperative. Therefore, the temperature range is limited capping the overall efficiency of the steam cycle. Molten salt mixture was used to increase the energy conversion efficiency and reduce the cost of electricity production (Bauer, *et al.*, 2010). Several physical and thermodynamic properties of thermal energy play significant role in determaining the efficiency and performance of waste heat recovery system. The three parameter which directly affect the thermal energy capacity in system are melting point, thermal stability and heat capacity where these parameter most important feature to consider in the system for heat transfer applications. From the previous literature there are large amount of melting point data available for various molten salt system with melting point less than 120 ºC is very limited. From all the previous study on molten salt system revealed that five group of molten salt are emphasized and commonly used alkaline nitrate/nitrite, carbonates, sulphates, chlorides and hydroxide.

2.2 Overview of Molten Salt and Applications

Components or compounds such as sodium nitrate salt can be written in general as $M^+X^-$where X^- is the anion and M^+ is a cation. In general, the selection of materials compatibility characteristics usually control the choice of anion for example fluoride, chloride, nitrate and so on. The option of cations usually controlled by other presentation issues such as the characterization of physical and thermal properties. Some examples of molten salt components are Berrylium fluoride (BeF_2), Magnesium chloride ($MgCl_2$), Sodium borohydride ($NaBF_4$) and Pottasium nitrate (KNO_3).

Salt mixture composed of different individuals salt components are mixed together into a multi-component system as a binary mixture, ternary mixtures or quaternary mixture. The melting point of the individual components should be high for any application. Mixing of several components to the system binaries, ternary or quaternary salt can reduces the melting point of the resulting system to a more practical level. Each mixture has a specific composition depends on the different parts of each component in the mixture. Each of the mixtures and compositions have physical properties and chemical different, and therefore the molten salt is optional depending on the type of application.

Applications of molten salt can be seen in thermal energy storage. Thermal energy storage (TES) has been designed to meet the power dispatchable load profiles with middle and high value benefits to utility power. The two groups of sensible heat storage are solid such as. concrete, rock, ceramicsand for liquid like water and molten salt (Thomas Bauer, Breidenbach, & Eck 2010). Intermittent nature of solar energy is required in the TES system for the most efficient use of this energy source. TES system functioned as a reservoir of energy to collect and transfer the heat energy of Heat Transfer Fluid (HTF) for media storage. Thermal energy normally collected by the parabolic trough, then transferred to the storage of heat by heat transfer fluid and subsequently transferred to the steam generator storage media. To enable the storage of thermal energy in the system directly, the heat transfer fluid will collect solar heat that serves as a storage medium. The cost of solar power systems is dependent on the properties of the heat storage medium and heat transfer fluids (Reddy, 2011).

Other research presented focused on molten salt storage for concentrated solar power plants. Molten salt is the best candidate because they have the advantage of a high heat capacity, high density, high thermal stability and low cost, and it is also known for its excellent heat transfer characteristics for use in thermal storage. This application has become important in the thermal technologies for solar energy concentration (Villada *et al*., 2014). System using molten salt as the heat transfer fluid and for the thermal storage has been proposed for solar thermal power generation. The use of molten salt as the heat transfer fluid because it is cheaper, compact, and can store more energy per volume of oil-based HTFs. Additionally it also offers good storage conditions. The other advantages of the molten salt is i) pollute less, ii) not flammable, iii) more abundant iv) has a lower vapor pressure, v) offer cost savings due to smaller heat tank and pipes (Sniderman, 2012). Of the overall research on the various properties of the material, molten salt is a very special group that has great potential as thermal energy storage and heat transfer media for solar energy applications. Molten salt, on the other side can be used at high temperatures above 500 ºC and it does not indicate one of the dangers and serious manner even have characteristics good heat transfer. Normally, salt used is a mixture of sodium and potassium nitrate and sodium nitrate, commonly referred to as a heat transfer fluid (Singh, 1985). Furthermore, molten salt is significantly less costly than the oil based HTFs currently used and allows for long term storage for heat.

Another application of molten salt is waste heat recovery. Waste heat can be interpreted as heat rejected from a facility to the environment. Recovery and reuse of this heat has the potential for reducing energy cost. Waste heat recovery system in which waste heat fluid, such as flue gasses, through a heat exchanger configured to transfer energy in the form of heat to the heat transfer fluid, preferably molten salt (Jeremy, *et al*., 2010). Energy in molten salt is used to generate usable energy such as electricity. In other words, a waste heat recovery system, which consists of liquid waste heat sources where the first heat exchanger configured to transfer heat energy from waste liquid to liquid heat transfer while the second heat exchanger configured to transfer energy from the heat transfer fluid to the working fluid; and energy production system is configured to convert the energy transferred in the working fluid into electrical energy (Jeremy, Xie, & Safe, 2010). Figure 2.1 shows the molten salt system as heat transfer fluid.

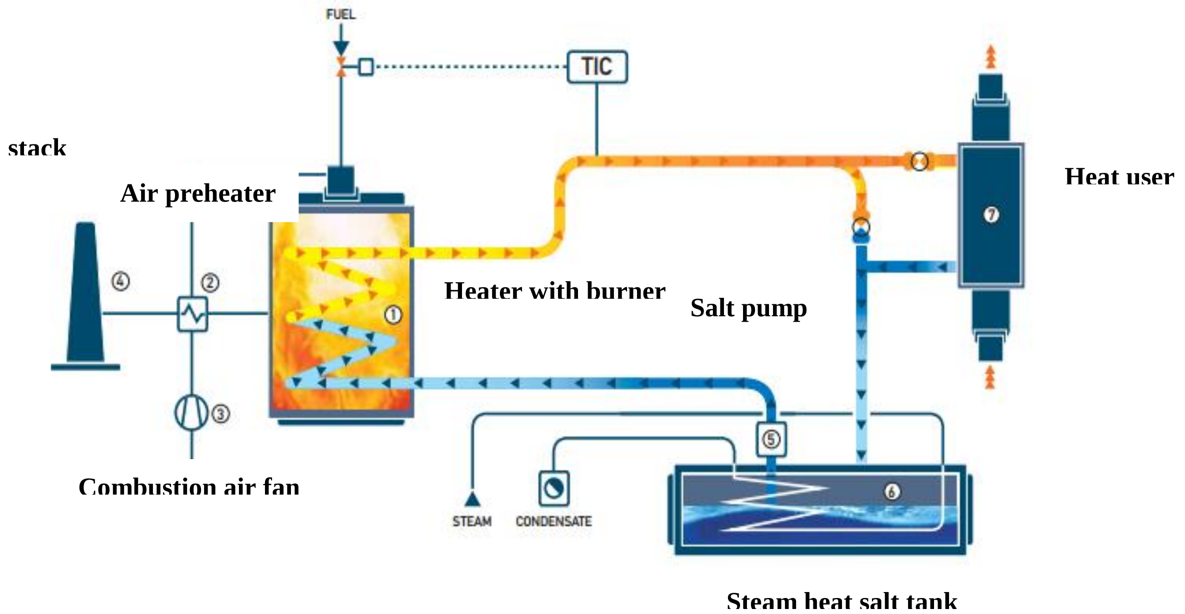

Figure 2.1 Molten salt system (Jeremy, *et al.*, 2010).

2.3 Melting Point

2.3.1 Melting point for various salt

From the previous researcher, there are large amount of melting point data available for various molten salt system. From the previous also, it was found those with melting point less than 120 ºC is very limited. All the previous study on molten salt system revealed that five group of molten salt are commonly used. That is alkaline nitrates, carbonates, sulphates, chlorides and hydroxide. Nowadays focuses on expanding the database of thermophysical properties of alkali and alkaline earth cations with nitrate or nitrite anions. Previous reports discuss low-melting salts containing lithium, sodium, potassium and calcium cations with nitrate and nitrite anions. The main method of thermal decomposition of these nitrate salt was agreed by many researchers such as Freeman (1956) and Sirotkin (1959). Recent developments in multi-component molten salt consisting of alkali and alkaline earth nitrates have the appropriate characteristic to be applied as heat transfer fluid in waste heat recovery system. The melting points of individual and multi components nitrate/nitrite system are listed in Table 2.1 (Peng, *et al.*, 2010).

Table 2.1 Melting point of various nitrate salt systems (Peng, *et al.*, 2010).

Compound	Melting point (ºC)
$LiNO_3$	253
$NaNO_3$	307
KNO_3	334
$Ca(NO_3)_2$	561
$Sr(NO_3)_2$	570
$Ba(NO_3)_2$	590
$NaNO_3$-$NaNO_2$	221
$NaNO_3$-$NaNO_2$-KNO_3	141
$NaNO_3$-KNO_3-$CaNO_3$	133
$LiNO_3$-KNO_3-$NaNO_3$	120
KNO_3-$CaNO_3$-$LiNO_3$	117
$LiNO_3$-KNO_3-$NHNO_3$	92
KNO_3-$NHNO_3$-$AgNO_3$	52
$LiNO_3$-$NaNO_2$-$NaNO_3$-KNO_3	99

Different from the nitrate salt, for carbonate system that list in Table 2.2 (Peng, *et al.*, 2010) the melting point for both the individual and multi component carbonate system are on the higher side. For this carbonate system, lowest melting point was achieved with lithium, sodium and pottasium ternary system where the melting point is 277 ºC that is higher than nitrate ternary system with the same cation (Marionwski & Maru, 1977). Caused by thermal decomposition issues, the selection of components for the carbonate system is very limited and some salt like $CaCO_3$ doesn’t have stable form at high temperature and the lack of multi-component system reduces the chance of the synthesis of low melting point salt mixtures. Although this group is not stable salt heat and working temperature range is relatively small, but it is still seen as the candidate can work at a high temperature because of low prices.

Table 2.2. Melting point of various carbonate salt systems (Peng, *et al.*, 2010)

Compound	Melting Point (ºC)
Li_2CO_3	732
Na_2CO_3	858
K_2CO_3	900
MgCO3	990
Na_2CO_3-K_2CO_3	710
Li_2CO_3-Na_2CO_3	496
Li_2CO_3-K_2CO_3	488
Li_2CO_3-K_2CO_3-Na_2CO_3	397

Alkali and alkaline fluoride/chloride salts are also selected as one possible choice as heat transfer fluid in solar energy and the melting point from the previous literature are given in Table 2.3 (Mayo, 1971). A lot of study has be done for this molten salt group and found the the melting point for this group is the same range with carbonate group but for the pure salt, metal chloride salt have a low

Table 2.3 Melting point of various fluoride/chloride salt systems (Mayo, 1971).

Compound	Melting Point (ºC)
LiF	849
NaF	996
KF	858
LiCl	610
NaCl	801
KCl	771
LiF-KF	493
LiF-NaF	652
LiCl-KF	487
LiF-NaF-KF	454
LiF-NaF-KF-MgF_2	449
LiF-KF-BaF_2	320
LiF-KF-CsF-RbF	256

2.3.2 Melting temperature for molten salt based on nitrate/nitrite system

Application molten salt as the heat transfer fluid is considered by the lower temperature limit and is determined by the melting temperature. The main challenge with molten salt is to be frozen during the operation. Therefore alkali nitrate and nitrite is a good candidate because of the low melting and excellent heat capacity. Nitrate salts were selected for use because of their favorable properties compared with other candidates. Commercially, molten salt heat transfer fluid previously found to have a high melting point, typically 140 °C or more. The liquid molten salt compositions include novel materials which consist of a mixture of lithium nitrate salts, sodium, potassium, cesium, and calcium. This unique mix can exploit eutectic behavior and cause the low melting at 65 °C and the thermal stability limit over 500 °C (Raade & Padowitz, 2011). Several molten salt heat transfer fluids have been used for solar thermal systems. Table 2.4 shows a systematic list of the melting temperature of single salt and the minimum melting temperature of salt system with cations calcium (Ca), pottasium (K), lithium (Li), and sodium (Na) and the anions nitrate (NO_3) and nitrite (NO_2) using previous sources (Bauer, Laing, & Tamme, 2011).

Table 2.4 Matrix of (minimum) melting temperature of subsystems of the reciprocal system Ca,K,Li,Na//NO_2,NO_3 (Bauer, *et al.*, 2011)

	NO_2	NO_3	NO_2,NO_3
Single salt and binary system with common action			
Ca	398ºC#	561ºC#	393ºC
K	440ºC	334ºC	316-323ºC
Li	220ºC	254ºC	196ºC
Na	275ºC	306ºC	226-233ºC
Binary systems with common anion and ternary reciprocal)			
Ca,K	185ºC	145-174ºC	130ºC
Ca,Li	205-235ºC	235ºC	178ºC
Ca,Na	200-223ºC	226-230ºC	154ºC
K,Li	98ºC	126ºC	94ºC
K,Na	225ºC	222ºC	142ºC
Li,Na	151ºC	196ºC	126ºC
Ternary additive common anion and quaternary reciprocal			
Ca,K,Li	N/A	117ºC	N/A
Ca,K,Na	N/A	130ºC	N/A
Ca,Li,Na	N/A	170ºC	N/A
K,Li,Na	N/A	119ºC	N/A
Quaternary additive common anion and quinary reciprocal			
Ca,K,Li,Na	N/A	109ºC	N/A

Decomposition at melting temperature

Based on the table above the melting temperature of the single salt is between 220 °C ($LiNO_2$) to 561 °C ($Ca(NO_3)_2$. Compared to single salt, more salt mixture showed the advantages of lower melting temperature. Therefore, a mixture of salt may have a wider temperature range than a single salt.

2.4 Heat capacity

For heating process, the temperature of molten salt increase by absorbing energy a substance to the substance's increase in temperature. Conversely, in the cooling process, which is the same as the amount of heat released or used in the development of heating systems. In other words, heat capacity is the amount of heat required to increased the temperature of certain material by 1 ºC and for large heat capacity assures the efficiency of the application.

2.4.1 Heat capacity for various salt

From the previous researcher, the heat capacity alkali/alkaline nitarte was investigated for both individual and multi-component system to simplify the comparison, between various type of salt the heat capacity value to differentiate the various salt as heat transfer fluid and shown in the following table. Among those alkali nitrate salt system it shown that $LiNO_3$ has a large heat capacity while KNO_3 present the lowest value. It can be seen in Table 2.5 which shown the heat capacity result for various compound of salt.

Table 2.5 Heat capacity of various nitrate salt systems (Marianowski & Maru, 1977)

Compound	Heat capacity (J/g.K)
$LiNO_3$	2.175
$NaNO_3$	1.686
KNO_3	1.400
$NaNO_3$-KNO_3-	1.533
$LiNO_3$-KNO_3	1.642
$LiNO_3$-KNO_3-$NaNO_3$	1.681
$LiNO_3$-$NaNO_2$-$NaNO_3$-KNO_3	1.689

Completely different with carbonate salt system, the heat capacity is almost constant and independent with temperature (Marianowski & Maru, 1977). For pure carbonate salt, the heat capacity shown decrease, which means the value for lithium carbonates is largest and pottasium carbonates is smallest. It can seen in Table 2.6 the result of heat capacity value for carbonate salt. The value of heat capacity for carbonate salt when melt is larger than solid state but when carbonate in binary system the value of heat capacity in solid is larger than liquid state (Wang, 2011).

Table 2.6 Heat capacity of various carbonate salt systems (Marianowski & Maru, 1977)

Compound	Heat capacity (J/g.K)
Li_2CO_3	2.50
Na_2CO_3	1.78
K_2CO_3	1.51
Na_2CO_3-K_2CO_3	1.57
Li_2CO_3-K_2CO_3	1.60
Li_2CO_3-Na_2CO_3	2.09
Li_2CO_3-K_2CO_3-Na_2CO_3	1.63

Besides carbonate and nitrate, the study of fluoride/chloride was also studied by previous researcher as Takahashi (1985) to compared with other types of salt available. The value for heat capacity fluoride/chloride shown in Table 2.7. Same with carbonate salt system, the value of heat capacity shown the salt contain lithium halide have a biggest capacity compared than pottasium halide is smallest. This fluoride/chloride salt have smallest value in liquid state.

Table 2.7 Heat capacity of various fluoride/chloride salt systems (Takahashi, 1985)

Compound	Heat capacity (J/g.K)
LiCl	1.48
NaCl	1.15
KCl	0.90
LiF-KF	1.63
NaCl-$MgCl_2$	1.00
LiF-NaF-KF	1.55
KCl-$MgCl_2$-$CaCl_2$	0.92
LiF-NaF-KF-MgF2	1.55

In summary, based on the various salt above the molten salt based on nitrate shown the high capacity compared than carbonate, fluoride/chloride including pure salt, binary salt, ternary salt or quaternary. Molten nitrate salt is suitable to applied as heat transfer fluid in any application.

2.5 Thermal stability for various salt

The general finding that molten salt mixture based on nitrate is stable up to temperature 500 ºC. This advanced HTF developed as a result of the discovery process in which a mixture of materials inspection nitrate salts have low melting points and are stable at temperatures of at least 500 °C based on the properties, including the composition, melting point, and thermal stability (Suite, 2010). The thermal decomposition processes of nitrates and nitrites were summarized by Stern, (2010). From previous review the thermal stability of the salt was detemined by using thermal gravimetric analysis (TGA). The decomposition temperature depends on various aspects include the definition itself, the experimental method (e.g. sensitivity, heating rate), crucible material and atmosphere. Figure 2.2 show results of TGA of single nitrate and nitrite salts, as well as four mixtures with a low melting temperature (Bauer *et.al.*, 2010.)

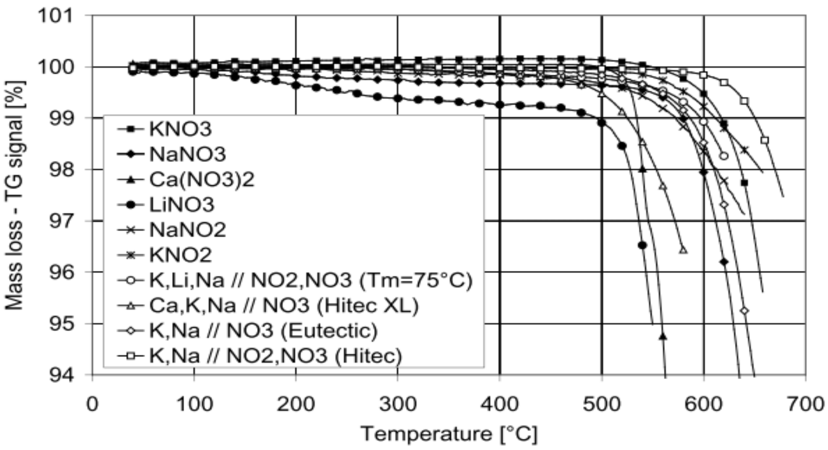

Figure 2.2 TGA measurementof single alkali nitrate salts (filled symbols) and alkali nitrite salts (asterisk symbol) and salt mixture (open symbol) (Bauer *et.al*., 2010).

For carbonate mixture and the salt was investigated the eutectic Li_2CO_3–Na_2CO_3–K_2CO_3 in the proportions 32.1–33.4–34.5 wt.% and the study was done by simultaneous using TGA it was found that the thermal stability is stable up more 1000 ºC but the melting point of this mixture is quite high at between 401 ºC and 405 ºC. Even molten salt from carbonate have a high thermal stability and this characteristic is the one criteria for heat transfer fluid but compared than nitrate, mixture from carbonate salt have a higher melting point. The addition of carbonate is not expected to significantly alter the stability of the nitrate because the interaction between carbonate and nitrate is very weak. Through simple eutectic phase diagram from Figure 2.3(a) and Figure 2.3(b) shown there is no stable compounds are formed between KNO_3-K_2CO_3 and $NaNO_3$-Na_2CO_3. Therefore, the addition of carbonates is not expected to change the stability of nitrates significantly and the molten salt mixture based on nitrate is more stable up.

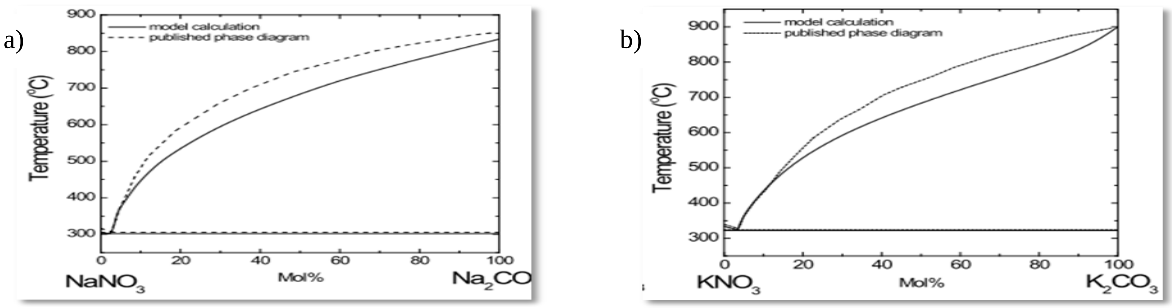

Figure 2.3 Published phase diagrams for the a) $NaNO_3$-Na_2CO_3 and b) KNO_3-K_2CO_3 systems (Levin *et al.*, 1964)

2.6 State of the art alkali nitrate/nitrite salt mixtures

There are various state of the art salt mixtures for concentrated solar energy and other applications. In particular, molten salt used in solar energy is KNO_3-$NaNO_3$. Other salt mixtures are also used including KNO_3-$NaNO_3$-$NaNO_2$ with trade names HITEC, Durferrit, ASD or HTS. $Ca(NO_3)_2$-KNO_3-$NaNO_3$ with trade name HitecXL also used in solar energy. Table2.8 showed the overview of alkali nitrate/nitrite salt mixture that used in solar energy and other application. Use nitrate salt as heat transfer fluid are potential candidates to replace the current hydrocarbon fluids or something else used in solar application. Nitrate mixtures are stable at very high temperatures (~500°C), have negligible vapor pressures, are environmentally benign, and have low viscosities at working temperature.

Table 2.8 Overview of alkali nitrate/nitrite salt mixture (Bauer, Laing, & Tamme, 2011)

Classification	Example
State of the art alkali nitrate/nitrite mixtures	
Single salt	$NaNO_3$, KNO_3
Binary system, common anion	KNO_3-$NaNO_3$)
Ternary additive, common anion	$Ca(NO_3)_2$-KNO_3-$NaNO_3$
Ternary reciprocal	K, Na // NO_2, NO_3
Novel alkali nitrate/nitrite mixtures	
Quaternary additive, common. anion	$Ca(NO_3)_2$-KNO_3-$LiNO_3$-$NaNO_3$
Quaternary reciprocal	Li, Na, K // NO_2, NO_3

2.7 Eutectic mixture

In a eutectic mixture exhibits the lowest melting point from any of the same mixture with the same components. The change in Gibbs free energy ΔG of a substance on the melting temperature T can be expressed in terms of changes in the exothermic enthalpy and entropy changes in ΔS.

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

At equilibrium, $\Delta G = 0$ and the melting temperature can be expressed as

$$T = \frac{\Delta H}{\Delta S} \qquad (2)$$

Eutectic mixtures tend to reducing the change in enthalpy or to increase the change in entropy. Binary mixtures, ternary or even more dramatically quartenary a behavior in a eutectic mixture. There have been significant work done on modeling the phase behaviour for binary, ternary and quaternary mixture of salt (Lin *et al.*,1979). Therefore, the development and synthesis of various molten salt mixture should be reviewed in order to obtain a lower freezing point than the molten salt mixture used previously as a heat transfer application. This is necessary for higher efficiency and getting rid of any unnecessary cost.

In nitrate salt mixtures, eutectic points exist, where at specific chemical composition, the system solidifies at a low temperature at any other composition. At the eutectic point also, two component of the liquid mixture is in equilibrium and each of component is crystals but if the temperature is lower past the eutectic temperature, each component will begin to crystallize out of mixture (Prigogine & Defay, 1973). In paper by author (Prigogine & Defay, 1973) also stated with using a salt with at or a near eutectic composition will have a lower melting point, high thermal stability ang high heat capacity than for instance using a pure salt.

2.7.1 Binary mixture

This mixture system is probably most studied but for the detail phase diagram are not yet agreed. To understand the mechanisms involved to improve the functioning of the nitrate salt mixture it is important to identify the thermal properties of pure components and binary mixtures KNO_3-$NaNO_3$ known as binary systems and molten salt mixture of commercial and critical for some applications such as transfer fluid which acts as a heat storage medium in the molten salt TES tank (Laue, 1998). $NaNO_3$ melts at 307 ºC and KNO_3 melts at 337 ºC. The results of this study have been published more than 40 papers since 1857. Figure 2.4 showed the summarizes some phase diagrams of the KNO_3-$NaNO_3$ system. A suitable mixture of pure reagent grade KNO_3-$NaNO_3$ in the weight proportions 54.33 wt% - 45.67 wt%.

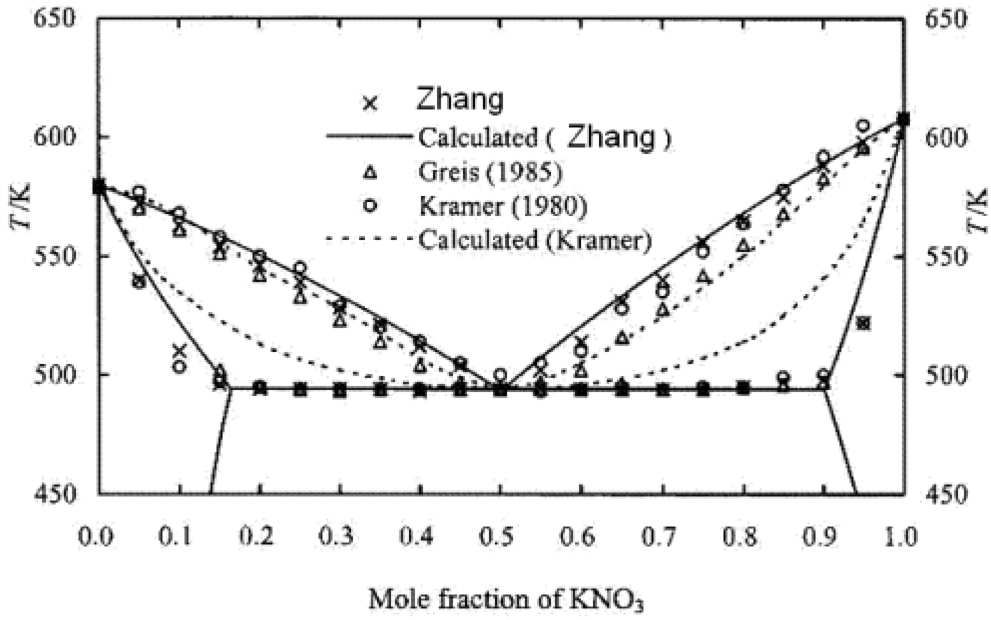

Figure 2.4 Overview of different phase diagrams of the system KNO_3-$NaNO_3$
(Zhang, X., *et al.*, 2003)

From the Figure 2.4 shows the proportion of the solidus and liquidus among the authors. Based on the recent literature, it is generally agreed that the composition of KNO_3 (50 mol%)-NaNO3 (50 mol%) or by weight KNO_3 (54 wt%)-$NaNO_3$ (46 wt%) fortunately there has always been agreement that the minimum melting point was close to 220 °C (Berg & Kerridge 2004). For binary mixture of 60% by weight of $NaNO_3$ and 40% by weight KNO_3, the figure shows a solar salt is not mixed in the minimum melt temperature rather it shows the condition two phases between solid and liquid. Usually, this binary system has a melting point 221 ºC (Bauer *et al.*, 2010). Although this salt mixture have no lowest melting point, but it still emphasized because of its low investment cost. There are some drawbacks for this binary nitrate mixture where in evening or winter this molten salt easily to freeze and will block the pipeline. From that, it can caused some auxiliary cost should be added to handle this problem and the investment will increased.

From the general findings, that the binary KNO_3-$NaNO_3$ molten salt mixture is stable up to temperatures of 500°C and only little weight change of the melt, although over this temperature there was some evolved NO_x gases. Another one of the most studied additives for heat transfer fluid is lithium nitrate or $LiNO_3$ assumed to improve the performance of molten salts, extending temperature work range regarding with a low melting point as well as a higher thermal stability.

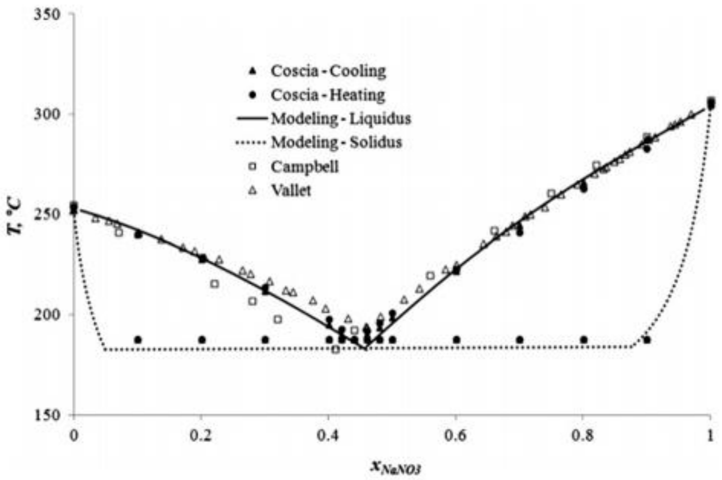

Figure 2.5 Phase diagrams of the system $LiNO_3$-$NaNO_3$

The phase diagram for the $LiNO_3$-$NaNO_3$ binary system is shown in Figure 2.5. Experimentally determined that the eutectic temperature for this binary system was 196 ºC at a composition of 44 mol% $NaNO_3$ and 56 mol% $LiNO_3$. The calculated eutectic point was determined at a composition of 46 mol. % NaNO3 and a melting point of 183 º C.

2.7.2 Ternary mixture

Ternary mixtures of $NaNO_3$ and KNO_3 with other alkali and alkaline earth nitrates have much lower melting points than the binary salt mixture. Eutectic behaviour and more drastic melting point reduction occurs with more complex salt mixture such as ternary. The ternary reciprocal system KNa//NO_2NO_3 has been examined by a number of authors. The author Alexander and Hindin (1947) found vitrification for KNO_2 have rich compositions. Alexander & Hindin (1947) found for NO_2 vitrification with different compositions. Most publications agree on the composition of the molten minimum equal to the minimum diagonal section of KNO_3-$NaNO_2$. Minimum molten mixture is usually defined as KNO_3 (53 wt%)-$NaNO_2$ (40wt%)-NaNO3 (7 wt%), or KNO_3 (44 mol%) - $NaNO_2$ (49 mol%)-$NaNO_3$ (7 mol%). This mixture has been used since 1973 as a heat transfer medium and the melting temperature of this mixture is 142 °C.

There have been numerous studies and patents reported in the literature on melt chemisteries to reduce the eutectic temperature of potassium-nitrate and sodium nitrate (Kramer & Wilson, 1980). Besides that, extending the upper working temperature by adding the other salt or controlling the nitrate to nitrite ratio. (Cordaro & Rubin, 2010). Consequently, in this work, have studied new heat transfer fluids with various additions of $Ca(NO_3)_2$ and $LiNO_3$, with the aim of replacing the binary salt that is currently used to improve the characteristic of heat transfer. Bradshaw and Siegel (2009) highlighted that addition or replace of $LiNO_3$ in ternary system in KNO_3-$NaNO_2$-$NaNO_3$ its suitable characteristic in improving the range of thermal stability of salt, although the main problem associated with this additive its price. Table 2.9 show the melting temeperature and thermal stability with different composition from another researcher in ternary mixture that always used. According to the researcher Reddy, (2011), the heat capacity for the ternary mixture of $LiNO_3$-$NaNO_3$-KNO_3 salt. the heat capacity in liquid state becomes very stable and increase with temperature linearly with little slope. Figure 2.6 shown the heat capacity curve where the value are measured after phase transformation or after melting of the salts.

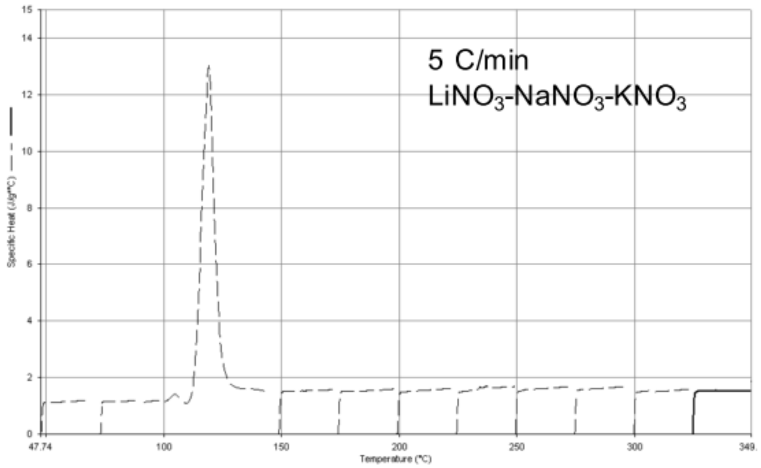

Figure.2.6 Heat capacity data plot of $LiNO_3$-$NaNO_3$-KNO_3 ternary system. (Reddy, 2011)

Table 2.9 Melting temperature and thermal stability of $LiNO_3$-$NaNO_3$-KNO_3 ternary system with different composition. (Bradshaw &Siegel 2009)

$LiNO_3$	KNO_3	$NaNO_3$	Melting temeperature ºC	Thermal stability ºC	Author, Year and Reference
25.9 wt%	54.1 wt%	20 wt%	118	>435	(Reddy,2011)
30 wt%	18 wt%	52 wt%	120	>550	(Bradshaw, 1990)
25.9 wt%	20.06 wt%	54.1 wt%	118	>500	(Wang .T., Mantha.D. &Ramana G.R, 2013)

$Ca(NO_3)_2$ is one of the additives that shows the most promise for solar energy. Its low cost and capacity to reduce the melting point of alkaline nitrates demonstrate the enormous potential of the additive to be included in new formulations of molten salts for energy storage and make it a primary candidate to substitute the binary solar salts. Another of system is $Ca(NO_3)_2$-KNO_3-$NaNO_3$ and this is a ternary additive system with the common anion NO_3. Bergman *et al*., (1955), published ternary phase diagrams as in Figure 2.7 of this system and found the minimum melting temperature of this system with value 160 ºC. A patent also claims this mixture with a melting temperature of 130 °C. In general it can be said that there is some discrepancy in the composition of the minimum melting mixture but the minimum melting temeperature by Bergman *et al*., (1955) are closely. Table 2.10 show the melting temeperature with different composition from another researcher.

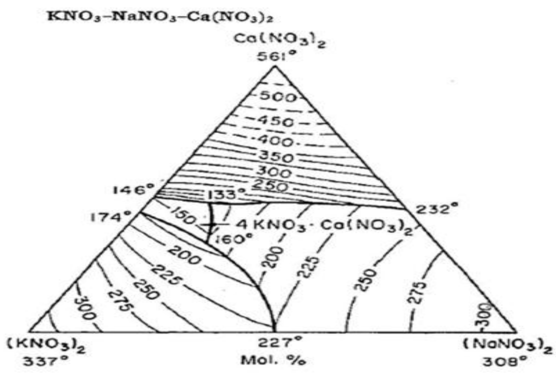

Figure 2.7 $Ca(NO_3)_2$-KNO_3-$NaNO_3$ ternary diagram (Bergman *et al*.,1955).

Table 2.10 Literature review of the minimum melting temperature and composition of the system $Ca(NO_3)_2$-KNO_3-$NaNO_3$.

Min. Liquidus Temperature	$Ca(NO_3)_2$	KNO_3	$NaNO_3$	Author, Year and Reference
175 °C	42 wt%	43 wt%	15 wt%	(Menzies & Dutt, 1911)
130 °C	63 wt%	27 wt%	10 wt%	(Jänecke, 1942)
133 °C	61 wt%	30 wt%	9 wt%	(Bergman, 1955)
160 °C	47 wt%	40 wt%	13 wt%	(Bergman, 1955)
130 °C	44 wt%	44 wt%	12 wt%	(Patent 1982)
120 - 190 °C	16 - 48 wt%	43 – 50 wt%	7 - 34 wt%	(Bradshaw, 1990)

Based on the contents of Table 2.10 minimum melting composition shown by Janeck (1942) and Bergman *et al*.,(1955), shows the composition of the mixture of $Ca(NO_3)_2$ is reduced and the composition is increased in KNO_3. Reduction of $Ca(NO_3)_2$ this maybe to improve the stability of the mixture as $Ca(NO_3)_2$ is less stable nitrate. Another ternary nitrate salt mixtures consisting of 50–80 wt% KNO_3 0 –25 wt% $LiNO_3$ 10–45 wt% $Ca(NO_3)_2$ melts below 100 ºC and thermal stability is up to 500 ºC. Stern, (2010) reported decomposition pressure, or as an alternative to the equilibrium constant, to improve as follows $KNO_3 < NaNO_3 < Ca(NO_3)_2 < LiNO_3$ (highest stability for KNO_3). In paper of (Stern, 2010) also stated that nitrite is considered less stable than the nitrate.

2.7.3 Quaternary mixture

Several molten salt have been used as heat transfer fluid including binary mixture, ternary mixture and more dramatically is quaternary mixture. The potential for improving the salt resides in optimising its physiochemical properties, mainly its melting point, thermal stability and heat capacity, by developing new quaternary mixtures or by incorporating novel components. The currently available molten salt formulations do not provide an optimum combination of properties, melting point, high thermal stability, high capacity and also cost that is needed for a replacement heat transfer fluid in waste heat recovery system. Therefore, this study also examines the design quaternary mixture of molten nitrate innovative, with the goal of improve solar salt is used at present as heat transfer fluid in solar energy. Inspection of published phase diagram, revealed that ternary mixture of $NaNO_3$ and KNO_3 with several alkali and alkaline earth nitrates have quite low melting point. This quaternary salt, which contains different weight percentages of $NaNO_3$, KNO_3, $LiNO_3$ and $Ca(NO_3)_2$, exhibits better physical and chemical properties than the binary solar salt (60 wt% $NaNO_3$-40 wt% KNO_3) currently used. In several light studies from Wang *et al*.,(2013), where involved the $LiNO_3$ and $Ca(NO_3)_2$ the researcher propose a new quaternary mixture with a composition of 10 wt% $LiNO_3$+20 wt% $NaNO_3$+60 wt% KNO_3+10 wt% $Ca(NO_3)_2$. From the researcher Bradshaw *et al*., (2009) is known to disclose anhydrous compositions mixture belonging to the quaternary $LiNO_3$-$NaNO_3$-KNO_3-$Ca(NO_3)_2$ system, said this compositions having a melting temperature below or closely 95 °C and a high thermal stability up to the temperature of 500 °C. Molten salt mixtures which containing calcium nitrate and lithium nitrate lowers the melting point of a salt mixture based on sodium nitrate and potassium nitrate. The transition observed in the thermal study the KNO_3 content at temperatures above 300 ºC did not properly melt with the other components and the signal coincides with values reported in the literature and experimental values obtained for the melting of potassium nitrate (Fernandez *et al*., 2012). The maximum stability for this mixture is 580.36 ºC with decomposition starting 469.56 ºC and have shown in Figure 2.8. From the figure defined the maximum stability temperature as the temperature at which the sample, after being stabilised via the elimination of water, lost 3% of its overall weight. Heat transfer fluid made of a mixture of four inorganic nitrate salts including 9-18 wt% $NaNO_3$,40-52 wt% KNO_3, 13-21 wt% $LiNO_3$, and 20-27 wt% $Ca(NO_3)_2$ can have liquidus temperatures less than 100° C (Bradshaw, 1990).

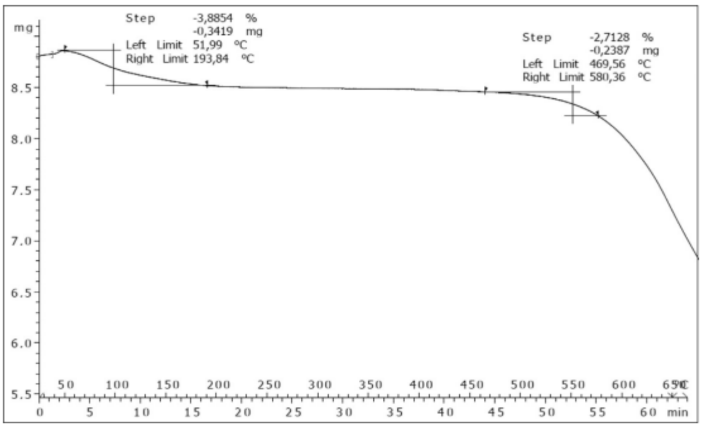

Figure 2.8 Thermal decomposition curve of $LiNO_3$-$Ca(NO_3)_2$-$NaNO_3$-KNO_3 mixture (Bradshaw *et al*., 2009)

From the previous researcher also studied for this quaternary mixture of heat capacity, the analyse performed using the modulated DSC and revealed the heat capacity is 1.518 J/g ºC and which have improvement over heat capacity binary mixture currently used (Kearney & Mahoney, 2002). This finding is notable because the newly designed salt is able to store more energy at a lower volume of salt.

2.8 Performance molten salt as heat transfer

With the rapid economic development and the improvement of living standards of energy use also increased rapidly and because of that energy shortage become terribly severe. Heat transfer fluids based molten salt is one medium that is used at present as one of type of liquid heat carrier has a direct effect on this solar energy system. At present, heat transfer medium in solar energy are used by binary molten salt, ternary system or quaternary system (Peng *et al.*, 2010). All these mixed systems have different thermophysical properties and have been discussed in previous studies in which the potential for improving the salt resides in optimising their thermophysical properties such as melting point,thermal stability and heat capacity can be improving by developed the new composition of each component but maintaining the relative proportions. Compared with heat conduct oil, molten nitrate salt have environmentally friendly, non-flammable, and also stable fluid. Alexander, (1947) had studied that ternary and quaternary nitrate salt was stable above 454.5 ºC.

2.9 Molten Salt as heat carrier in heat recovery system

At present, the low temperature heat recovery, including industrial waste heat, geothermal energy, solar thermal and biomass can be a very critical and sustainable to resolve the energy crisis. Waste heat recovery through the application of Rankine cycle system is considered as an effective method of recovering the waste heat, as it aims to minimize the amount of heat wasted by the way of reusing it in either the same or a different process to produce a useful energy. Waste heat recovery system consists of fluid waste heat sources where the first heat exchanger configured to transfer heat energy from waste fluid to heat transfer fluid. The second heat exchanger is configured to transfer energy from the heat transfer fluid to the working fluid and normally, heat transfer fluid are used is molten salt taht has been recognized as a heat carrier liquid (Jeremy, *et al.*, 2010). Using waste heat along with attempts to use renewable resources as a low grade heat source heat has led to wider use of Organic Rankine Cycle. One example is preferably used as heat carrier is molten salt. In this system the molten salt mixture is used as the heat carrier fluid in the vary system. The most widely used system consists of a mixture of nitrate, potassium nitrate and calcium nitrat but depend on the thermophysical properties where have discussed in literature before. For this system, liquid waste heat will pass through a heat exchanger configured. The liquid are used to transfer energy in the form of heat to heat carrier in this system. By using molten salt as heat carrier do not need to be replaced, and do not exhibit the hydrogen permeation problem that oil-based HTFs exhibited.(Sniderman, ASME, 2012). Furthermore organic heat carrier cannot be used except molten salt can be used as heat carrier at low temperature, because low cost and efficient in store energy (Jagadees, 2011). In heat recovery system the energy in the molten salt is used to generate useable power such as electrical energy.

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