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

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ABSTRACT

Various materials such as water, oil heat, ionic liquids and also molten salt are selected to serve as heat transfer fluid. The nitrate based molten salt that has been use in this study consists of binary, ternary and quaternary salt mixture with different weight composition. DTA, TGA and DSC were performed to obtained melting point, thermal stability and heat capacity. The melting point for ternary and quaternary mixtures are closely 100 ºC compared than binary mixture. Quaternary mixture shown the highest result in thermal stability and heat capacity with the value 701 ºC and 4.7 J/g ºC and have fulfilled the targeted characteristic as heat transfer fluid.

Keywords: molten salt, binary, ternary, quaternary.

INTRODUCTION

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. Molten salt is used because it is a liquid at atmospheric pressure, non-flammable, low cost and efficient in store energy (Jagadees, 2011). 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, & Rafiq, 2012). 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). Therefore, a lower melting point in range of 60 - 120 ºC and a high thermal stability above 500 ºC are desired

Because some of these constraints, an alternative heat transfer fluids will be introduced to address the current HTF used with a mixture of inorganic salts based on nitrates with different salt constituents and different weight composition. Consequently, the three sytems of salt mixture has been studied consisting binary, ternary and quaternary with improving the salt resides in optimizing its physiochemical properties, mainly its melting point, thermal stability and heat capacity. Thermal analysis (DTA, TGA and DSC) has been done in order to obtain the melting point, thermal stability and heat capacity.

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.

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

At equilibrium, ΔG = 0 and the melting temperature can be expressed as:-

$$T = \frac{\Delta H}{\Delta S} \tag{2}$$

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.

In nitrate salt mixtures, eutectic points exist, where at specific chemical composition, the system solidifies at a low temperature at any other composition. The author (Prigogine & Defay, 1973) had explained 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. 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.

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. For this mixture, KNO_3-$NaNO_3$ are commercially used for some applications such as transfer

fluid which acts as a heat storage medium in the molten salt TES tank (Laue, 1998). Single salt of $NaNO_3$ melts at 307 ºC and KNO_3 melts at 337 ºC. The results of this binary mixture have been published more than 40 papers since 1857 and Figure 1 shown the phase diagram for this mixture that investigated by (Zhang, X., et .al, 2003). This figure shows the proportion of the solidus and liquidus and 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.

Different with binary mixture of 60% by weight (64 mol%) of $NaNO_3$ and 40% by weight (34mol) KNO_3 which had been investigated by Bauer, et. al., (2010) by using the same phase diagram in Figure-1 from Zhang, X., et .al, (2003) where this mixture has a melting point 221 ºC but from this figure showed this mixture salt not mixed in the minimum melt temperature rather it showed the condition two phases between solid and liquid.

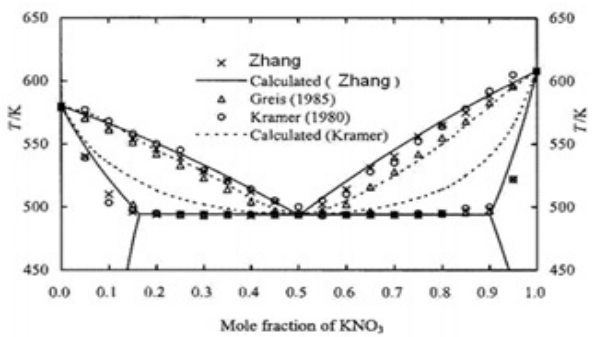

Figure-1. Overview of different phase diagrams of the system KNO_3-$NaNO_3$ (Zhang, X., *et al.* 2003).

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. The binary mixture of KNO_3-$NaNO_3$ also 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. In paper written by Fernández *et al.* (2012) addition or replaced of lithium nitrate or $LiNO_3$ with $NaNO_3$ can improve the performance of molten salt extending temperature work range regarding with a low melting point as well as a higher thermal stability.

Ternary mixture

Alexander & Hindin, (1947) found 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. In paper of (Cordaro & Rubin, 2010).propose extending the upper working temperature by adding the other salt or controlling the nitrate to nitrite ratio can reduce the melting point in binary mixture. For example 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.

Consequently, in this work, new heat transfer fluids with various additions of $Ca(NO_3)_2$ and/or $LiNO_3$, with replacing the binary salt that is currently used. Therefore, to reduce the melting point or improving the characteristic of salt mixture in binary mixture (Bradshaw & Siegel, 2009) have 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 is price. Bradshaw & Siegel, (2009) also have simplify into the Table-1 where the ternary mixture that always used.

Table-1. The melting temperature and thermal stability of $LiNO_3$-$NaNO_3$-KNO_3 ternary system with different composition. (Bradshaw &Siegel 2009).

$LiNO_3$ wt%	KNO_3 wt%	$NaNO_3$ wt%	Melt.temp °C	Thermal stability °C
25.9	54.1	20	118	>435
30	18	52	120	>550
25.9	20.06	54.1	118	>500

The one addition of molten salt where can reduced the melting point and gived improving to binary salt mixture is $Ca(NO_3)_2$. According to Bergman *et al.* (1955), $Ca(NO_3)_2$ is one of the additives that 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. The minimum melting temperature of this system that has been found with value 160 ºC.

Quaternary mixture

Several molten salt have been used in waste heat recovery system including binary mixture, ternary mixture and more dramatically is quaternary mixture. 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 solar fields. 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 waste heat recovery system. In the paper by 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% $Ca(NO_3)_2$ exhibits better physical and chemical properties than the binary solar salt currently used.

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 having a melting temperature below or closely 95 °C. and a high thermal stability up to the temperature of 500 °C. From another researcher that investigated by (Kearney & Mahoney, 2002) 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.

METHODOLOGY

Preparation of molten salt

Salt component that has been used are sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$) ,potassium nitrate (KNO_3), calcium nitrate-tetrahydrated ($Ca(NO_3)_2.4H_2O$ and lithium nitrate ($LiNO_3$). Each of the components contained in the anhydrous form has been ground with a mortar and pestle and dried in an oven at a temperature 115 °C for 12 hours. For calcium nitrate components obtained in the form of tetrahydrate and not dehydrated prior to melt.

Salt mixtures were formulated with the desired composition. The salt were mixing according to the different composition and have been reported in literature as the best formulation based on the melting temperature. Each mixture has a total mass 50g and this mass was used to characterize the thermophysical of salt mixture. Salt mixture have been studied in this paper consisting binary, ternary and quaternary mixture. The sample was heated in a furnace at a temperature of 150 ºC for 4 hours to dry the component and the temperature has been increased to 400 ºC for 8 hours to homogenize the sample. After melting, the sample need to maintain at temperature of 115 ºC for 1 hour before removed from furnace and cooled at room temperature. Then the salt mixtures have been ground into powder to be characterized by DSC, TGA and DTA

Apparatus and procedure

A Differential Thermal Analysis (DTA) was used to measure the melting point of the salt mixture. Salt mixture have been ground into powder using mortar and pestle because the salt mixture in lumpy conditions. Small amount range between 50–70 mg of the mixture are placed on the crucible with ramped ambient to 400 ºC at 15 °C/min using air as the purge gas.

After measuring the melting point, 50-70 mg of mixture are placed on crucible for Thermogravimetric Analysis (TGA) testing to obtained the thermal stability and the temperature was ramped from ambient to 900 ºC at 15 °C/min using air as the purge gas.

For heat capacity determination Differential Scanning Calorimetry (DSC) was used. Standard aluminium pan with lid used for DSC measurements are weighed before the experiment. Small amount range between 7-12 mg of the compound is placed carefully in the aluminium pan and closed with lid. The measurements were made under purified nitrogen atmosphere with a flow rate of 20cc/min and at a heating rate of 10 ºC/min.

RESULT AND DISCUSSION

Melting point

Figure-2 shows the result of melting point that have been simplify by using bar graph for binary, ternary and quaternary system.

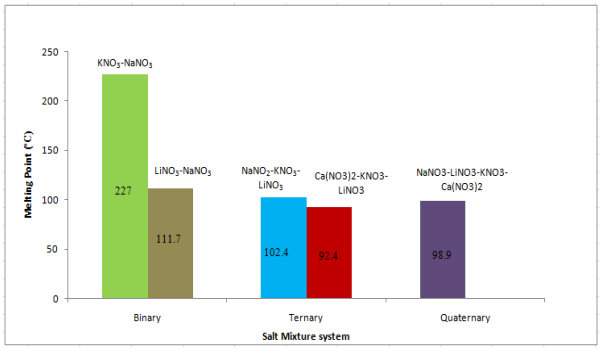

Figure-2. Melting point for all systems in ºC.

From the Figure-2 ternary and quaternary mixture shown the lower melting point value compared to binary mixtures with the value is closed to 100 ºC. Bradshaw *et al.* (2009) are stated in their paper that to disclose anhydrous compositions mixture belonging to the quaternary $LiNO_3$-$NaNO_3$-KNO_3-$Ca(NO_3)_2$ system, this compositions having a melting temperature below or closely 100 °C. But for binary mixture $NaNO_3$-$LiNO_3$ have reduced the melting point where the value is 111.7 ºC. According to Bradshaw & Siegel, (2009), with addition or replaced of $LiNO_3$ into binary mixture it can reduce the melting point of this system. In this paper also stated that replaced or controlling the nitrate to nitrite ratio can reduce the melting point where the value of melting point in ternary mixture for $NaNO_2$-KNO_3-$LiNO_3$ are lower

Thermal stability

Maximum temperature stability studied in this research is the temperature at which the sample undergoes stability after elimination of water. Raade & Padowitz, (2011) defined the high temperature thermal stability limit of the salt as that where the salt is observed to rapidly begin to lose weight. Molten salts based on nitrates exhibit many desirable heat transfer qualities at high thermal stability temperatures and for this study the value of thermal stability for all system shown the highest value above 500 ºC. Figure-3 shows the result of thermal stability and decomposition temperature for quaternary system that have been done by TGA testing where the value is 703 ºC and 588.4 ºC. From Figure-3 also the value

of thermal stability or where the rapid weight lose begin for quaternary system shown the highest value above 500 ºC. In the work of Raade & Padowitz, (2011) also stated the potential for improving the physiochemical properties mainly the thermal stability are by developing the new quaternary mixtures or by incorporating novel components.

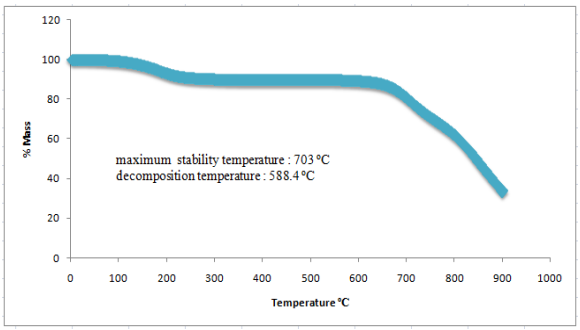

Figure-3. TGA plot for quaternary mixture.

Decomposition temperature for all systems shows the value increased with thermal stability value. In some studies of Freeman, (1956) has been reported the decomposition temperature is the temperature at which the substance chemically decomposes and they also investigated that decomposition reactions are major concern for high thermal stability. With increasing the nitrite content, reduces the activity of NO_3 in the melt and hence limits the extent of the decomposition, which increases the upper temperature of the stability range.

Heat capacity

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. In this study, binary and ternary mixture given the low heat capacity value compared than the quaternary mixture. Figure-4 shows the result of heat capacity for quaternary mixture. It is noted that heat capacity is an average of specific heat capacities for temperature between solid and liquid transitions.

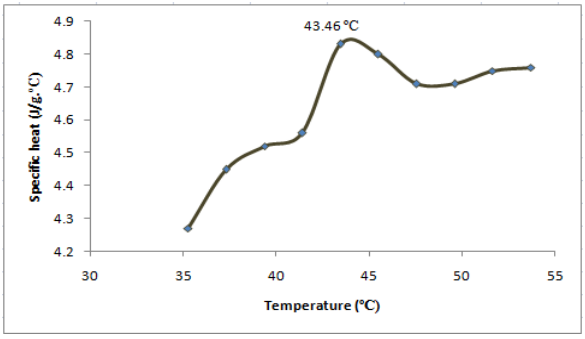

Figure-4. DSC plot for quaternary mixture.

Figure-5 shown the heat capacity value by using bar graph for all mixture. In general, it can be expected for the heat capacity of the binary mixture to be a weighted average of the single nitrates. Both Jriri *et al.*(1995) and Ichikawa *et al.* (1983) reported values for these nitrates very similar to each other and to the ones of the binary mixture with other additives mixture It shown different value with ternary system where the value is high compared than binary mixture.

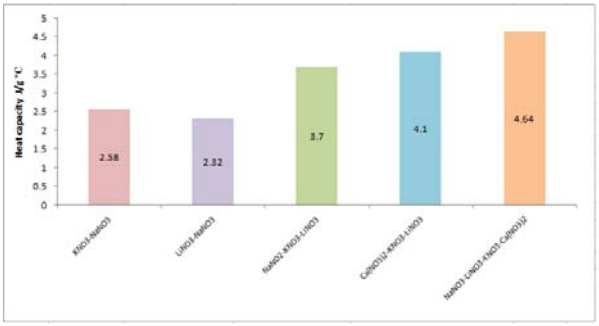

Figure-5. Heat capacity value for all salt mixture in J/g ºC.

In overall, the value for quaternary mixture is very high compared to binary and ternary which the value is 4.64 J/g ºC. This mixture is able to keep the high heat capacity even in low temperature compared to binary and ternary mixture which keep the heat capacity to high temperature. Furthermore, in previous findings from Chhabara, (2010) have stated that molten salts freeze at relatively high temperature with range 120 ºC to 220 ºC.

CONCLUSIONS

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. A lower melting point in range of 60 - 120 ºC and a high thermal stability above 500 ºC and large heat capacity are desired for enhance the efficiency as heat transfer fluid for waste heat recovery system The melting point for ternary and quaternary mixtures are closely 100 ºC compared than binary mixture. Quaternary mixture shown the highest result in thermal stability and heat capacity with the value 701 ºC and 4.7 J/g ºC and have fulfilled the targeted characteristic as heat transfer fluid.

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