Effect of lithium nitrate and calcium nitrate composition on the thermal properties of quaternary molten salts mixture for heat transfer application

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Abstract. Mixed molten salt is considered as a promising medium for both heat transfer and energy storage in thermal power because of its many advantages such as low the melting point, large heat capacity, good thermal stability and low cost. In order to determine the thermal properties of the molten salt, the nitrate quaternary mixture of the molten salt are prepared based on the different composition of the lithium nitrate and calcium nitrate. The other salts in the mixture are potassium nitrate and sodium nitrate. Mixture of molten salts were heated in furnace at 150°C for 4 hours and increased the temperature to 400°C for 8 hours for homogenize the salt mixture. Then, decreased the temperature to 115°C for an hour. The melting point and thermal stability of the mixture was determined by using thermogravimetric analysis [TGA] while the heat capacity was determined by using differential scanning calorimetry [DSC]. The lowest melting point using different composition of lithium nitrate, 10wt%NaNO₃, 40wt%KNO₃, 20wt%Ca(NO₃)₂, 30wt%LiNO₃ which is 97.1°C while the heat capacity is 6.33 J/g°C. For the experiment using various composition of calcium nitrate, the lowest melting point is from 14wt% NaNO₃ + 48wt% KNO₃ + 13wt% LiNO₃ + 25wt% Ca(NO₃)₂ which is 111.7°C and the heat capacity is 2.06 J/g °C. From the result, the addition of lithium nitrate in the quaternary molten salts give more effect to the reduction of melting point value but higher heat capacity.

1. Introduction
Molten salt is a means of storing heat at a high temperature. Molten salt is constituting of potassium nitrate, calcium nitrate, sodium nitrate, lithium nitrate. It has the property to absorb heat and to store the heat energy that is released to the water to transfer energy when needed. Molten salt that have high thermal energy storage capacity will increase the efficiency and enhance the performance for thermal energy storage. Thermal energy storage capacity of a salt mixture is dependent on melting point, density and specific heat capacity. Lower the melting point, more efficiency the molten salt. Then for thermal stability of the salt mixtures plays an important role in determining its utility as a potential thermal energy storage media.

Nitrate mixtures and mixtures of nitrate and nitrite are being used in the applications because of low melting point, low unit cost, high heat capacity and moderate density which imply excellent energy storage capability. Binary mixtures of alkali molten nitrates or nitrites present phase diagrams with a
simple eutectic point. By adding one or more components, it is expected that the resulting mixture will have a lower melting point compared to the initial eutectic binary mixture. In this direction, the design of multicomponent mixtures by the addition of alkali/alkaline earth nitrates will make more working temperature range of thermal energy storage. The additives that present greater potential to be used for solar energy storage are Ca(NO₃)₂ and LiNO₃ because these salts decrease the melting point and improve the thermal stability, respectively. Other researcher proposed the study of molten salts of more than three components approach to achieve an effect between the properties calcium nitrate, Ca(NO₃)₂ and lithium nitrate, LiNO₃ of additives and the components of the solar salt. The most notable property of the molten salts using calcium and lithium nitrate is its energy density which is based on the heat capacity, which represents an important improvement over the solar salt currently used. Based on this parameter, a smaller amount of salt could be used to store the same amount of energy.

Most of the existing commercial solar thermal power plants currently use synthetic oil as the heat transport fluid in the collector field. It offers a very low freezing point less than 0°C and tolerable temperature limit 393°C among those available heat transfer fluids. The removal of the oil to nitrate salt, heat exchangers also reduces the unit storage system costs. Such as direct system would assistance impressively from a reformed parabolic through system such as the Super trough describe by Kolb and Diver [1]. The possessions of molten nitrate salt mixtures as heat transfer fluids for solar thermal systems are estimated, at the same time as the focus is placed on the melting temperature of salt mixtures with varieties compositions. In addition, enhance molten salt composition will beneficial for a wide range of industrial development heat applications.

Binary mixture and ternary mixture was used as heat transfer fluid in several molten salt but the most efficient mixture is from quaternary mixture. developing quaternary mixture will improve the performance of salt drastically. Researcher found that KNO₃-NaNO₃ with other several alkali nitrate has quite low melting point. So they proposed new formulation of quaternary mixture with composition 10 wt% LiNO₃ + 20 wt% NaNO₃ + 60 wt% KNO₃ + 10 wt% Ca(NO₃)₂. The composition of this system having melting point below or closely 95°C and high thermal stability up to 500°C.

Research from [2] state that heat transfer fluid made of mixture of four inorganic nitrate salts including 9-18 wt% NaNO₃, 40-52 wt% KNO₃, 13-21 wt% LiNO₃ and 20-27 wt% Ca(NO₃)₂ can have liquidus temperature less than 100°C. Based on [3], the research revealed that ternary mixture of molten salt which 63.7 wt% KNO₃, 27.3 wt% Ca(NO₃)₂, 9.0 wt% LiNO₃ having 76°C as melting point temperature. In their paper, the melting point, heat capacity and chemical stability and viscosity of molten salt mixtures were measure through experiments. Besides that, heat capacity curve shows at about 150°C. This means the composition cannot form the eutectic at about 80°C. It may because of operational of a freezing-up if the temperature drops unexpectedly. According to the [4], 16 kinds of mixed nitrate were prepared based on different mass proportions of KNO₃-LiNO₃-NaNO₃-Ca(NO₃)₂·4H₂O. The melting point of the samples were obtained by analysing the heating DSC curve. Melting point Nos. 12 until 16 are about 80°C.

Quaternary mixtures are mixtures consisting of four nitrate salt mixture used as liquid energy storage. In previous study state that quaternary mixtures are more effective compared to binary and ternary mixtures because of it low melting temperature condition. Thus, this study contributes to examines the design quaternary mixture of molten nitrate innovative, with the goal to improve solar salt is used at present as heat transfer fluid in solar energy. The quaternary salt involved which contains different weight percentages of NaNO₃, KNO₃, LiNO₃, and Ca(NO₃)₂, exhibits better physical and chemical properties than the binary solar salt. In several light studies [5],where involved the LiNO₃ and Ca(NO₃)₂. From the other researcher [6] is known to disclose anhydrous compositions mixture belonging to the quaternary LiNO₃-NaNO₃-KNO₃-Ca(NO₃)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 mixture 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 KNO₃ content temperature above 300°C 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 [7]. Therefore, in this studied and proposed new heat transfer fluids [HTFs] with various additions of Ca[NO₃]₂, with the objective of replacing the binary salt that is currently used. The heat capacity will increase slightly if the mixtures is added by the calcium nitrate and lithium nitrate. The calcium nitrate heat capacity an approximate value is 120-140 J/mol/K by previous researcher [8].

In general, the development of the molten salt preparation is important in order to find the molten salt mixture with low melting point and wide usable temperature. As the mentioned above is greatly effort of development of molten salt as heat transfer fluid and storage technology. Therefore, this study will determine the effect of lithium nitrate and calcium nitrate in nitrate quaternary molten salt in order to develop low melting point and high heat capacity of molten salts as heat transfer fluid in heat recovery system.

2. Methodology

2.1. Preparation of mixture

The primary salt that used in this research are sodium nitrate NaNO₃, potassium nitrate KNO₃, calcium nitrate tetrahydrated Ca[NO₃]₂·4H₂O and lithium nitrate LiNO₃. For those salt, it is found in the form of anhydrous except for calcium nitrate which is tetrahydrate and not dehydrated before melted. The percentage of weight for each component of salt in the quaternary mixture were developed. The salt is placed into the container and weighed according to its position. The mass of all the salt mixture is the same which is 50 grams. Table 2.1 shows the mass of the component is according to their percentage.

After weighed each component of the salt, the four salt were mixed all together. Then the sample of mixture was heated in a furnace at 150°C for 4 hours for the drying process. The process will continue by increased the temperature to 400°C for 8 hours for homogenization process to ensure homogenous between each of salt. Then the sample will be take out from the furnace and cooled the sample at the surrounding temperature.

Table 2.1 Mass of the component according to percentage with addition of calcium nitrate.

| Sample | Mixture Composition (wt%) | Weight (g) |
|--------|---------------------------|------------|
| Sample 1 | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 20 + 48 + 22 + 10 | 10 + 24 + 11 + 5 |
| Sample 2 | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 22 + 40 + 23 + 15 | 11 + 20 + 11.5 + 7.5 |
| Sample 3 | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 10 + 50 + 20 + 20 | 5 + 25 + 10 + 10 |
| Sample 4 | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 14 + 48 + 13 + 25 | 7 + 24 + 6.5 + 12.5 |

Table 2.2 Mass of the component according to percentage with addition of lithium nitrate.

| Sample | Mixture Composition (wt%) | Weight (g) |
|--------|---------------------------|------------|
| Sample A | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 10 + 60 + 10 + 20 | 5 + 30 + 5 + 10 |
| Sample B | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 10 + 50 + 20 + 20 | 5 + 25 + 10 + 10 |
| Sample C | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 10 + 40 + 30 + 20 | 5 + 20 + 15 + 10 |
| Sample D | NaNO₃+KNO₃+LiNO₃+Ca(NO₃)₂ 10 + 30 + 40 + 20 | 5 + 15 + 20 + 10 |

2.2. Characterization of molten salt

The characteristic of all sample of mixture will be measured and analysed. Thermodynamic properties were measured including melting point, heat capacity and thermal stability. For this research, Differential Scanning Calorimetry [DSC] and Thermogravimetric Analysis [TGA] is used. Differential
Scanning Calorimetry [DSC] have been used to study or test the heat capacity of the sample of mixture while Thermogravimetric analysis have been used to determine the melting point and thermal stability of the molten salt.

3. Result and discussion

3.1. Discussion of result to the effect of lithium nitrate
Melting point is one of the characteristic of the molten salt as the heat transfer fluid and one of the properties that need to determine in this project. Melting point is when the salt mixture starts to melt and liquid is form. Figure 1 shows the melting point for all samples quaternary mixture various of Lithium Nitrate.

![Melting Point for All Sample Quaternary Mixture Various of Lithium Nitrate](image)

Many researchers found that molten salt that contain four inorganic nitrate salt having low melting point. This statement was confirmed by [2] that stating that molten salt with four different composition of nitrate salt can reach temperature below than 100°C and their paper also state that by addition or replace of LiNO3 is suitable and can lower the melting point. Besides that, other researchers found that this quaternary molten salt has a low melting point and can be approaching 95°C. However, the melting temperature of quaternary mixture for sample A which is 10wt%NaNO3, 60wt%KNO3, 20wt%Ca(NO3)2, 10wt%LiNO3 is 113.8°C.

Composition of molten salt mixture for sample A and B are the same with composition of molten salt that was done by [4]. The melting point for sample 2 which is 10wt%NaNO3, 50wt%KNO3, 20wt%Ca(NO3)2, 20wt%LiNO3 obtained from this mixture is 97.4°C. For sample C and D, the development composition of the mixture is to make a variety of composition and to see the behaviour of the molten salt if we are adding more composition of lithium nitrate to the mixture. The mixture for sample C and D is 10wt%NaNO3, 50wt%KNO3, 20wt%Ca(NO3)2, 20wt%LiNO3, 10wt%LiNO3 and 10wt%NaNO3, 50wt%KNO3, 20wt%Ca(NO3)2, 20wt%LiNO3 respectively. The melting point obtained from the result is 97.1°C and 112.7°C respectively. Sample C is lowest melting point compared to others mixture.

According to [4], their paper reported that the melting point of this both composition of molten salt is 80.4°C and 82.2°C respectively. Lithium nitrate which contain in the mixture is actually help the mixture to force melting point based sodium, potassium and calcium nitrate to the lower point. The result obtained is differ from the researchers maybe because the percentage usage of potassium nitrate is too high compared to others three salt. The melting temperature of potassium nitrate also high. According to [9] state that the potassium nitrate content did not melt completely with other salts at temperature above 300°C.
For the heat capacity, heat capacity is the amount of heat energy a unit of matter can hold. Definition also same with the amount of heat required to increase temperature of material. All material shows this increase in heat capacity with temperature. It is measured in unit J/mol or J/g.

**Figure 2. Heat Capacity Value of Liquid Phase in J/g °C**

Figure 2 shows the value of heat capacity for the quaternary mixture of molten salts. From the result above, it shows that heat capacity for the sample A and B are lowest compared to the sample C and D. The recent research the addition of lithium nitrate can lower the melting point and provide high heat capacity. So it can be concluded that sample C and D can be considered as best composition of the quaternary molten salt.

For thermal stability, thermal stability is another important characteristic of quaternary mixture molten salt in order to look its behaviour and to determine best composition of quaternary mixture molten salt as heat transfer fluid. Generally, the reaction occur in the process is the endothermic reaction. This is due to break down the bonds that holding the reactant and the energy will obtain as the new bond are formed. In the endothermic reaction, the energy that we obtained is less than the energy we put on it.

**Figure 3. TG curve for sample C**

From the TG curve (Figure 3), its shows the number of mass loss difference is not much. According to the [10], in their paper research stated that the mass losses with gas evolution of alkali metal nitrate salts may occur due to three reason that is nitrite formation in the melt and oxygen release, alkali metal oxide formation in the melt and nitrogen/nitrogen oxide release and vaporization of the nitrate salts. In their research also gives information about the aspects that affect the decomposition temperature. For examples is the method when conducted the experimental which is the value of heating rate is important
parameter to be considered. Other than that is crucible material and atmosphere. Most measurement of thermal stability of the molten salt, the mass losses occur at temperature range 500 °C up to 600 °C.

3.2. Discussion result to the effect of calcium nitrate
The transition in each composition between solid to liquid is very high for a small sample of a substance and it can be measured to 0.1 °C. Quaternary system gives a much lower melting temperature than binary and ternary systems. In recent studies have proved that mixture of NaNO₃-KNO₃ shows high melting point in the mixture. This is because, there is no low melting point in this system that have been reported by Berg & Kerridge [2004] state the minimum melting point stood close to 220°C for this salt mixture [11]. Figure 4 shows the melting point for all sample quaternary mixture several of calcium nitrate. The composition for sample 1 shows the higher melting point compared to sample 2, sample 3 and sample 4. The result for sample 1 which the composition is 20wt% NaNO₃ + 48wt% KNO₃ + 22wt% LiNO₃ + 10wt% Ca(NO₃)₂ shows the higher temperature of 122.6 °C in the mixture. It is because this composition having a large amount of potassium nitrate and sodium nitrate. In recent research state that NaNO₃ and KNO₃ with higher range wt% will increase the melting point of the system [12]. The addition of Ca(NO₃)₂ and LiNO₃ in specific range of 13-22 wt% LiNO₃ and 10-27 wt% Ca(NO₃)₂ was obtained in this studies resulted the greater potential to improving the lower melting point which both salt mixture can be depressing melting point for the molten salt system. It have been proved that NaNO₃-KNO₃-LiNO₃-Ca(NO₃)₂ system which known as quaternary composition having a melting temperature closely to 130°C [12]. In this project, the lowest melting point are found in the sample 4 which 14wt% NaNO₃ + 48wt% KNO₃ + 13wt% LiNO₃ + 25wt% Ca(NO₃)₂ with value of melting point is 111.8 °C.

![Figure 4. Melting Point for All Sample Quaternary Mixture Various composition of Calcium Nitrate](image)

For thermal stability and heat capacity determination, the thermal stability result was obtained in this study by using TG curve of quaternary mixture system. This curve also can determine the decomposition temperature of molten salt mixtures in the system which is known as temperature at which the substance is chemically decomposed. The reaction generally endothermic system as heat is required to break the chemical bonds in the compound undergoing decomposition.
Figure 5. TG curve for salt mixture sample 3: 10wt% NaNO₃ + 50wt% KNO₃ + 20wt% LiNO₃ + 20wt% Ca(NO₃)₂

Decomposition temperature is an important parameter for setting the maximum usable temperature which can be obtained from TG curve. This comparison of the sample mixture shows sample 1 with the rapid weight loss begin at 300.1 °C with the composition temperature for this sample is 58.5 °C. For sample 2 shows the maximum stability temperature at 322.8 °C with it decomposition temperature starts at 42.71 °C. Figure 5 shows TG curve for sample 3 of quaternary system. The maximum stability temperature with the rapid weight loss begin at 339.18 °C followed by decomposition temperature at 38.59 °C. Maximum stability temperature in sample 4 shows the rapid weight loss begin at 348.93 °C and the decomposition temperature started at 36.55 °C. For quaternary curve illustrated the small curved at initial temperature where it is referred as the transition and transformations that occur which can be seen that was caused by the loss of water at initial temperature.

This study proves the elimination of water will undergo by the stability of the sample mixture will produced maximum temperature stability in the systems. In the previous studies state that the thermal stability of the sample was defined as the temperature at which the sample had loss up to 1.2% of it mass due to strongly hygroscopic property and interior moister and impurities contained in this kind of molten salt [4]. Hence, there is relatively large mass loss was observed in the cycle that is mainly contribute the presence of impurities and also moisture which is arise from the atmosphere in the process of the sample. The moisture and impurities mostly were removed during the cycle and the mass loss is attributable to the decomposition of the salt component [13]. The curve seen to reach the equilibrium state at certain amount of time that is closely to 500 °C which undergoes in this quaternary salt system. The thermal stability can be improved with additive of Ca(NO₃)₂ in nitrate system and it is suitable in improving the range of thermal stability as state by the recent research [2].
Figure 6. Heat Capacity Value of Quaternary Mixture various composition of Calcium Nitrate

For heat capacity, value of heat capacity was determined by using the differential scanning calorimetry. The result of four samples mixture shown in the bar graph (Figure 6). This evaluation curved in DSC graph is to determine an average of specific heat capacities for temperatures between the solid-liquid transitions for four salt mixtures in this system. From all the system sample 3 shows the lowest heat capacity which is 1.78 J/g°C compare to the other three salt mixture. Sample 1 and sample 4 shows heat capacity 2.08 and 2.06 respectively which is not much different between them. In recent studies the higher heat capacity value of the quaternary salt system indicates greater potential of energy storage capacity for the solar thermal energy storage applications [13]. In solid state, mobility is low due to the rigid arrangement and the specific heat is mostly determined by vibration effect while in liquid state, the huge amount increase of specific heat is attributed the higher mobility which result of improvement of fluidity.

The statement was approved that in addition of LiNO₃ and Ca(NO₃)₂ into formula mixtures are able to reduce the melting point, improve the thermal stability and heat capacity of mixtures which can makes the resulting high heat capacity where it can see in this quaternary system [14]. It is important feature in molten salt system as heat transfer fluid that specific heat must be able to storing the greatest possible amount of energy as the lowest possible temperature in the salt system.

4. Conclusion

For the conclusion of this project, aim of this study were achieved which is to determine the best molten salt composition with various of lithium nitrate and calcium nitrate in order to develop lower the melting point, high heat capacity and good thermal stability molten salts as heat transfer fluid in heat recovery system. It is important to highlight that lithium nitrate and calcium nitrate containing with other two nitrate salt which is potassium and sodium can give best performance as thermal storage and heat transfer fluid because of its lower melting point. Lower melting point can be obtaining based on the composition of each salt to become mixture. Each mixture has their own physical and chemical properties that to be discussed.

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