Characterization and Thermal Properties of Nitrate Based Molten Salt for Heat Recovery System

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Abstract. Molten salt can acts like a storage medium or heat transfer fluid in heat recovery system. Heat transfer fluid is a fluid that has the capability to deliver heat this one side to another while heat recovery system is a system that transfers heat to produce energy. This studies shows about determining the new formulation of different molten nitrate/nitrite salts consisting of LiNO\textsubscript{3}, KNO\textsubscript{2}, KNO\textsubscript{3} and NaNO\textsubscript{2} that give a low temperature of melting point and high average specific heat capacity. Mixed alkaline molten nitrate/nitrite salt can act as a heat transfer fluid due to their advantageous in terms of its properties that feasible in heat recovery system such as high specific heat capacity, low vapour pressure, low cost and wide range of temperature in its application. The mixing of these primary substances will form a new line of quaternary nitrate salt (LiNO\textsubscript{3} - KNO\textsubscript{2} - KNO\textsubscript{3}- NaNO\textsubscript{2}). The quaternary mixture was heated inside the box furnace at 150\textdegree C for four hours and rose up the temperature to 400\textdegree C for eight hours to homogenize the mixture. Through heating process, the elements of nitrate/nitrite base were mixed completely. The temperature was then reduced to 115\textdegree C for several hours before removing the mixture from the furnace. The melting point of each sample were testified by using thermal gravimetric analysis, TGA/DTA and experiment of determining the specific heat capacity were conducted by using Differential Scanning Calorimeter, DSC. From the result, it is found that the melting point Sample 1 with percentage of weightage (25.4wt\% of LiNO\textsubscript{3}, 33.8wt\% of KNO\textsubscript{2}, 20.7wt\% of KNO\textsubscript{3} and 20.1wt\% of NaNO\textsubscript{2}) is 94.4\textdegree C whereas the average specific heat capacity was 1.0484/g\textdegree C while for Sample 3 with percentages of weightage (30.0wt\% of LiNO\textsubscript{3}, 50.2wt\% of KNO\textsubscript{2}, 3.1wt\% of KNO\textsubscript{3} and 16.7wt\% of NaNO\textsubscript{2}), the melting point is 86.1\textdegree C with average specific heat capacity of 0.7274 J/goC. In the nutshell, the quaternary mixture salts had been a good mixture with good thermal properties that low in melting point and have high specific heat capacity which could be a potential heat transfer fluid in heat recovery application.

1. Introduction
Molten salt technology is a combination of different technologies such as electro-chemistry, heat transfer, chemical oxidation or reduction baths and nuclear reactors. All of these applications are related by the common characteristics of molten salts which it can act as a mixture that has good specific heat capacity. Basically, the molten salt can produce an energy to the system while can withstand a high temperature course material [1]. According to Bradshaw \textit{et al.}, [2] molten salt heat
transfer is a compound that may enhance the thermal energy storage for a designated system. For further development according to this molten salt mixture that containing an alkaline nitrate and nitrite salts, both mixture have the advantageous properties that relevant in the application of energy recovery system. Bradshaw also state that molten salt have a very low vapour pressure and most inactive substances in the air [2].

Molten salt is both a non-toxic and inert liquid. It is frequently used as a heat transfer fluid as well as the thermal energy storage in different industries such as organic rankine cycle, concentrated solar power and electricity. According to Lu-di Zhang et al., [3] the usage of molten salts as a working fluid in industries might help in reducing the global warming by using solar system. Molten salts was very commercial in solar thermal power plant as heat transfer fluid and as a medium of thermal energy storage due to its advantages such as low viscosity, low vapor pressure, good chemical stability, low cost, wide range of operating temperature and environmental friendly [3]. According to US patent by Cordaro [4] and Bradshaw [5] molten salt is practically harmless substances in term of environmental surrounding. Also, it is stated that molten salt have a high density and high heat capacity that boosting the heat transfer capability. Besides, molten salt heat transfer fluid is a stable with contact with air and not a flammable substance.

One of the applications of molten salt is act as a heat transfer fluid. From previous researcher, the heat transfer fluids contain a high melting point and limit the practical application in concentrating solar power application [1, 6-11]. Quaternary molten salts are a mixture of four different salts that mixed well to be a new molten salt. To investigate the properties of thermal inside the system, quaternary salt is the most preferable mixture for previous researcher that can bring the best result of melting point, heat capacity and heat storage [6]. According to Wang et al., [6] a new quaternary mixture of LiNO₃ – NaNO₃ – KNO₃ – Ca(NO₂)₃ gives a better physical and chemical characteristic compare to binary Solar salt. At the end of these studies, the new compositions of quaternary nitrate salt that contain low melting point with high average specific heat capacity will be proposed for heat recovery system application.

2. Experimental Procedure
In order to find the best mixture of the quaternary nitrate salts, several composition were made by using the range of composition as shown in Table 2.1.

| Molten Salt | Range of composition |
|-------------|----------------------|
| LiNO₃       | 20-30 wt %           |
| KNO₂        | 30-52 wt %           |
| KNO₃        | 0-20 wt %            |
| NaNO₂       | 15-20 wt %           |

The mixtures of primary molten salt were prepared by following the range of composition listed on Table 2.1 to develop a new quaternary heat transfer fluid. By using the range of composition shown in Table 2.1, the new line of quaternary molten salt that gives low melting point has been determined. From this study, the low melting point of quaternary mixture is defined from 0 to 100°C whereas medium melting point is defined from 101 to 500°C. Meanwhile, high melting point is defined from 501°C and above. The nitrate based alkali was very famous among previous researcher since its gives a low temperature and high specific heat capacity in their application [3, 6, 12-14]. Table 2.2 shows that the mass ratio of sample 1, 2 and 3.
Table 2.2 The composition of molten salts in milligrams, (mg).

| No. sample | Mass in milligram (mg) | LiNO₃ | KNO₂ | KNO₃ | NaNO₂ |
|------------|------------------------|-------|------|------|-------|
| 1          | 25.4                   | 33.8  | 20.7 | 20.1 |
| 2          | 26.2                   | 46.3  | 10.0 | 17.5 |
| 3          | 30.0                   | 50.2  | 0.3  | 16.7 |

The mixing of quaternary molten salt was heated inside a box furnace. Firstly, the mixture of salt was heated at the temperature of 150°C for four hours to complete the process of removing existing moisture in the mixture. Then, the temperature was increased up to 400°C for eight hours to let the element well mixed. After the heating process was done for 8 hours, several hours was needed for the sample to go through cooling process until the temperature reached 115°C. Then, a new quaternary mixture was produced after exposing the mixture for several minutes at the room temperature. The phase of new quaternary molten salt after being exposed to the surrounding was solid phase. Then, the salt mixtures have been crushed into powder to proceed for the next step. The melting point of quaternary mixture was determined by using TGA/DTA machine. Meanwhile, we determined the specific heat capacity of the molten salt by using Differential Scanning Calorimeter, DSC.

3. Results and Discussion
In order to determine the melting point of each quaternary mixture, all sample were undergoes TGA/DTA testing. The result of melting point was detected on each peak of endothermic or exothermic peak that observed at DTA graph. The operating parameter that used for quaternary molten salt were, mass in milligram, (120-130mg), maximum temperature, (500°C), and temperature rise per minutes, (10°C/min). As for the quaternary molten salt result, Figure 3.1 shows the results of melting point of each mixture through TGA/DTA testing.

![Figure 3.1 Graph of Melting Point Versus Sample.](image)

From Figure 3.1, all three quaternary samples achieved the low temperature of melting point which is under 100°C. Based on the table 2.2, as the value of LiNO₃ increase, the melting point will decrease. According to previous researchers, by adding more LiNO₃ into the mixture will reduce the melting point of the molten salt [15] since LiNO₃ melts at lower temperature compared to other three primary
elements. So, it is important to increase the number of weight percentages, (%wt) of LiNO$_3$ in achieving a low temperature of melting point. Meanwhile, as the value of weightage KNO$_3$ decrease, the melting point will also decrease. According to Nan Ren et al., the sample gives a higher temperature due to the melting point of KNO$_3$ itself which was higher compared to other three elements [16]. Also, another researcher stated that the melting point of KNO$_3$ is higher than NaNO$_3$ which are 337°C and 307°C respectively [12]. By replacing or adding NaNO$_3$ into the mixture will help the molten salt to get a lower melting point. With this point, it is strong enough to be evidence that addition of KNO$_3$ will increase the melting point of the mixture. Next, as the weight of KNO$_2$ increase, the melting point will decrease whereas the melting points decrease as the mass of NaNO$_2$ decrease. By changing the nitrate solution to nitrite solution also can diminish the melting point [12] since its help molten salt to enhance the range of thermal stability of molten salt.

By completing the testing of DSC, the average results of specific heat capacity were then calculated. Differential scanning calorimeter (DSC) was conducted to provide the value of melting point and its specific heat capacity in the present of quaternary nitrate salt mixture [6]. Based on previous researcher, it is shows that the peak of the graph plotted was the value of specific heat capacity with its melting point [3, 6, 10, 13, 16-18]. From these results, the determination of formulation that contains low temperature and high specific heat capacity can be done. Figure 3.2 shows the graph of average specific heat capacity for three samples respectively.

![Figure 3.2 Average Specific Heat Capacities for Molten Salts.](image)

From Figure 3.2, the average specific heat capacity for Sample 1, Sample 2 and Sample 3 are 1.0484J/g°C, 0.7542J/g°C and 0.7274J/g°C respectively. Sample 1 shows that the average specific heat capacity was the highest while sample 3 shows the lowest value of average specific heat capacity. By referring Table 2.2, as the value of NaNO$_2$ decrease, the value of average specific heat capacity will also decrease. It is important to increase the value of NaNO$_2$ since it gives a higher value of average specific heat capacity. Also, as the value of LiNO$_3$ increase, the average specific heat capacity decrease. This is because LiNO$_3$ melts at a very low temperature [12] and has low specific heat capacity. Hence, by decreasing the value of LiNO$_3$ will increase the value of average specific heat capacity. In contrast, the quaternary mixture produce high average specific heat capacity compared to primary, binary and ternary mixture. Based on these three average specific heat capacities, Sample 1 gives the highest value compared to Sample 3 that gives the lowest value average specific heat capacity. It is mentioned that the higher the specific heat capacity, the greater the thermal stability that satisfied the application in thermal energy storage [6].
4. Conclusion
From result TGA/DTA testing, sample 3 of quaternary mixture give the lowest melting point which was 86.1°C but give the lowest value of specific heat capacity which was 0.7274 J/g°C. Besides that, sample 1, also give a low value of melting point which was 94.4°C but gives the highest value of specific heat capacity, 1.0484 J/g°C. For a conclusion, the best quaternary mixture molten salt that will be proposed was sample 1 that shows its properties in low melting point but high value in specific heat capacity. Hence, the aim of this study was fulfilled by finding the better formulation of molten salts in low temperature condition which are 25.4wt% of LiNO₃, 33.8wt% of KNO₂, 20.7wt% of KNO₃ and 20.1wt% of NaNO₂.

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