



Low Temperature Molten Salts in Sustainable Energy Production

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Abstract: Power production is moving towards more renewable energy sources with the aim of reducing CO₂ emissions. Examples of emerging technologies to meet this need include: concentrated solar power plants and liquid air energy storage systems. The overall system efficiency of such technologies can be increased by the introduction of a thermal energy storage system, to host excess heat and eventually to release it when needed. This work was focused on the identification of new molten salt mixtures as the thermal medium to act as both thermal energy storage and heat transfer fluid. Firstly, the thermo-physical properties of the commercial salt mixtures were reproduced using Aspen⁺, resulting in 5 nitrate-based mixtures providing the suitable trade-off between melting point temperatures and volumetric heat capacities. Secondly, 13 new salt compositions with improved volumetric heat capacities were created utilising the same constituents as the baseline mixtures, and then experimentally tested for the identification of the melting point. As a result, 4 alternative new molten salt mixtures, including 2 from the CaLiNaK family, were identified as preferred candidates due to higher improvements in volumetric heat capacity (15-19%) and only moderate increase in melting point temperature (20-30°C) with respect to the baseline mixture.

Keywords: *Molten salts; Melting point; Thermal energy storage; Heat transfer fluid*

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Nomenclature

CSP	Concentrated Solar Power	T_m	Melting Point Temperature [°C]
LAES	Liquid Air Energy Storage	c_v	Volumetric Heat Capacity [MJ/m ³ K]
TES	Thermal Energy Storage	c_p	Mass Heat Capacity [J/kgK]
HTF	Heat Transfer Fluid	ρ	Mass Density [kg/m ³]
wt%	Weight Fraction Percentage		

1. INTRODUCTION

Global warming has increased the focus of the power generation sector to reduce CO₂ emissions by utilizing lesser fossil fuels and greater renewable energy sources. The European Union has set a target for renewable energy to constitute 20% of the total energy produced by 2020 [1]. The very nature of renewable energy sources carries a series of intrinsic complexities in balancing the energy network, such as less flexibility and intermittent operation. Electric energy storage can partially mitigate these issues, allowing to charge energy when the production exceeds demand and to discharge it to the power grid when needed.

Amongst the technologies for sustainable energy production, two are gaining increasing interest from the research community: Concentrated Solar Power (CSP) and Liquid Air Energy Storage (LAES). CSP plants use a solar collector that reflects direct sun irradiation to a thermal receiver system, hence increasing the solar radiation flux density. This allows for higher temperatures and higher conversion efficiencies from optical energy to thermal energy [2]. During day time operation, surplus energy generated is stored in a Thermal Energy Storage (TES), which is used to heat the

working fluid of the thermal cycle during discharging, increasing the overall system efficiency. Moreover, a TES can increase the system reliability and reduce the energy cost for the customer.

An interesting solution for sustainable energy production is Liquid Air Energy Storage (LAES), which is gaining interest due to its advantages such as: large volumetric energy density, no geographical dependency, no pollution and long operative life [3]. LAES working principle is threefold: electrical energy is used to liquefy air via compression and refrigeration; cold liquefied air is stored in low pressure insulated tanks; when the grid requires additional power, liquid is drawn from the tank, heated and expanded in a turbine connected to a generator [4]. Similar to CSP plants, LAES employs a TES system, especially for the recovering of excess heat during the charging process (i.e. air liquefaction). It has been reported that, there is a 20-40% excess heat of compression, which currently is not being used effectively [5]. This thermal energy can be used to heat up the air during the discharging process (i.e. evaporation), hence increasing the overall system efficiency.

As the thermal medium for TES, molten salts have been investigated in the recent years due to their appealing features such as [6]: low melting point; high volumetric heat capacity; liquid over a wide operative temperature range etc. When compared against conventional coolants, they allow lower heat exchanger costs, as they provide volumetric heat capacities 25% higher than pressurised water and five times higher than liquid sodium. Moreover, they have been utilized as TES fluid in several CSP plants, including, USA (Solar Two), Spain (CESA I-PSA) and France (THEMIS) [7]. An interesting feature of such industrial applications is that, molten salts are also being used as the Heat Transfer Fluid (HTF), thereby reducing the system complexity.

This work is focused on the identification of new molten salt mixtures that offer low melting temperatures and beneficial thermo-physical properties in order to be used as both TES and HTF in the above applications. Firstly, screening of low melting point molten salt mixtures using the published literature was conducted, resulting in the down-selection of 5 baseline commercial salt mixtures for further investigation. Secondly, utilising the same constituents as the baseline mixtures, several new salt compositions were evaluated in terms of volumetric heat capacity using the Aspen⁺ simulation platform. Subsequently, experimental investigations were conducted to identify the melting point for 13 new mixtures. Finally, the combined evaluation of volumetric heat capacity and melting point lead to the identification of 4 alternative new molten salt mixtures.

2. SCREENING PROCESS

The aim of the present work was to investigate new molten salt mixtures for both TES and HTF. The melting temperature was chosen to be below 200°C, as it indicates the common temperature range for CSP and LAES applications. Table 1 presents the melting point screening results from the published literature on molten salts. The nitrate and chloride salt families offered comparable average melting point temperatures (113 vs. 108°C). Note that, solar salt is included as a reference due to its popularity in CSP plants.

As highlighted by Nunes et al. [9], there is a fragmentation in the published data on molten salt properties. Hence, a detailed literature review was conducted and a database of the most relevant thermo-physical properties was created. This database was imposed in Aspen⁺ to simulate the thermo-physical properties in the temperature range of application (100-400°C). For simulating salt mixtures, only the pure salt properties were imposed in Aspen⁺ using the database. Utilising the available published data on the commercial salt mixtures, Aspen⁺ property estimations were verified to give low errors (0.4%-13%).

The ability to reproduce the thermo-physical properties of the baseline commercial salt mixtures, using the database of pure salts, gave high confidence in estimating the thermo-physical properties not yet published in literature, for both the remaining commercial salt mixtures as well as the alternative weight compositions. This allowed to proceed with the second screening process, which was the evaluation of the overall thermo-physical properties in the temperature range. The most relevant of these properties being the volumetric heat capacity, as it governs the size of vessels and heat exchangers, and is calculated using the specific heat capacity and density as:

$$c_v = c_p \rho \quad (1)$$

Table 1 - Low melting point temperature of baseline commercial molten salts

Nitrates	T_m [°C]	Chloride	T_m [°C]	Reference	T_m [°C]
HITEC	142	NaCl-AlCl ₃	108	Solar Salt	222
LiNaK	120	KCl-AlCl ₃	128		
LiK	133	KCl-AlCl ₃ -NaCl	89		
Quaternary	99				
CaLiNaK	72				

Figure 1 presents the variation in volumetric heat capacity for the baseline commercial molten salt mixtures in the temperature range of application. It is evident how the chloride-based salt mixtures provided lower values of volumetric heat capacities compared to the nitrate-based salt mixtures (1.7-2.2 vs. 2.8-3.1 MJ/m³K). Hence, the chloride-based salt mixtures were disregarded from further consideration.

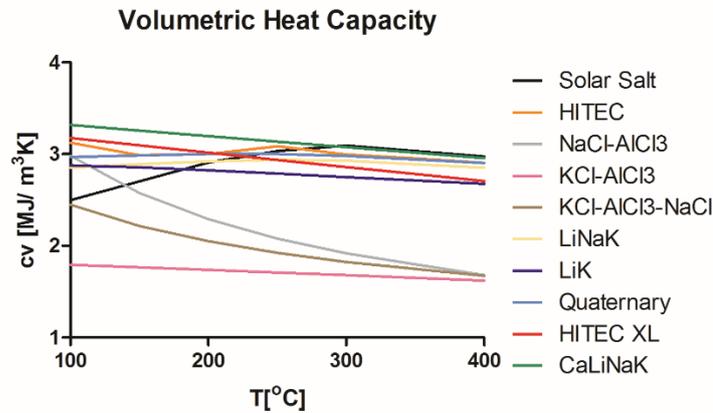


Figure 1 - Volumetric heat capacity variation of low melting temperature baseline commercial molten salts

The above screening process resulted in the down-selection of HITEC, LiNaK, LiK, Quaternary, CaLiNaK as the 5 baseline commercial salt mixtures for further investigation. Table 2 details the compositions of these molten salt mixtures expressed in mass fraction.

Table 2 - Down-selected 5 baseline molten salt mixture compositions expressed in mass fractions

Molten Salt Name	Composition
HITEC	7NaNO ₃ -40NaNO ₂ -53KNO ₃
LiNaK	28NaNO ₃ -52KNO ₃ -20LiNO ₃
LiK	68KNO ₃ -32LiNO ₃
Quaternary	14.2NaNO ₃ -50.5KNO ₃ -17.5LiNO ₃ -17.8NaNO ₂
CaLiNaK	24.6LiNO ₃ -13.6Ca(NO ₃) ₂ -16.8NaNO ₂ -45KNO ₂

3. EXPERIMENTAL MELTING POINT

New molten salt mixtures were simulated by varying the mass fractions of constituents in the 5 down-selected baseline commercial salts. For the parametric analysis, the variable of interest was the volumetric heat capacity. Two classifications of mixtures were considered: similar composition to baseline salt, and noticeably different composition to baseline salt but with a significantly higher volumetric heat capacity. As a result, a total of 13 alternative new molten salt mixtures were considered for experimental identification of melting point temperature. Additionally, any mass fraction variation that provided volumetric heat capacity lower than its baseline salt was disregarded from further consideration.

The experimental method included preparation of alternative salt mixture concentrations using the pure salts (KNO₃, NaNO₃, NaNO₂, LiNO₃, CaNO₃•4H₂O, 99% purity, Merck®). To ensure fine homogenous mixture, mass fractions were prepared using Kern® weighing scale (resolution 0.1 mg) and mixed using Camlab® vortex mixer. To limit errors relating to small weight fractions of pure salts, the minimum quantity prepared for salt mixtures was 5 grams.

For measuring the melting point, the Stuart® SMP3 was used. This allowed the simultaneous testing of three capillary samples (Stuart® OD/ID 1.9mm/1.3mm) with a fine control of the heating ramp rate. During testing of each mixture, a fast 5°C/min ramp rate was applied until the plateau temperature was reached, which was set at 30°C lower than the melting temperature of the baseline commercial salt mixture. Once the plateau temperature was reached, a slower 1°C/min ramp rate was applied. In order to gain enough precision, for each salt mixture, three tests were conducted and the mean values are reported. The melting temperature was calculated using the standard approach [10]:

$$T_m = \frac{T_{m,1} + T_{m,2}}{2} \quad (2)$$

where $T_{m,1}$ is the temperature at which the onset of melting was observed and $T_{m,2}$ is the temperature at which the samples were noted to be in a complete liquid state.

Particular attention was given to avoid air gaps and to ensure equal quantity of salt mixtures inside the tubes. The small tube size assured a favourable heat transfer to the salt mixtures due to the low thermal inertia. However, on occasions, this hindered the homogeneity of the sample, as some single salt clusters were observed separating from the salt mixture during testing.

Firstly, a validation of the experimental procedure was performed, with the aim of reproducing the melting points of the baseline commercial salt mixtures reported in the literature. Table 3 presents the experimental data for validation using the 5 down-selected baseline commercial salt mixtures. The HITEC, LiK and LiNaK results were reproduced within 1-3°C of the published values. However, a greater discrepancy was noted for the quaternary mixtures, with errors of 11-19°C. This may be attributed to a three-fold challenge. Firstly, the precision required for the individual components (e.g. mass fraction of 14.2 for NaNO_3 in Quaternary). Secondly, the complexity associated with an increased number of individual mixture components. Thirdly, due to the individual components purity being 99% (rather than 99.99%) to ensure an economical molten salt TES and HTF solution.

Table 3 - Experimental validation of melting point of the 5 down-selected baseline commercial salt mixtures using published literature

Molten Salt Name	Literature [T_m °C]	Experiment [T_m °C]	$[\Delta T$ °C]
HITEC	142	143	1
LiK	133	132	-1
LiNaK	120	123	3
Quaternary	99	118	-19
CaLiNaK	72	86	-11

Following the validation of the experimental procedure, tests were conducted on the two classifications of alternative salt mixtures. Figure 2 (a-c) presents the main field of view images during the successful testing of an alternative composition of LiNaK constituents. However, in limited number of cases, testing was discontinued as complete melting was not observed below 200°C. Thus, making the salt mixture unsuitable for the considered CSP and LAES applications. Figure 2 (d-f) presents such an unsuccessful testing example of an alternative composition of HITEC constituents.

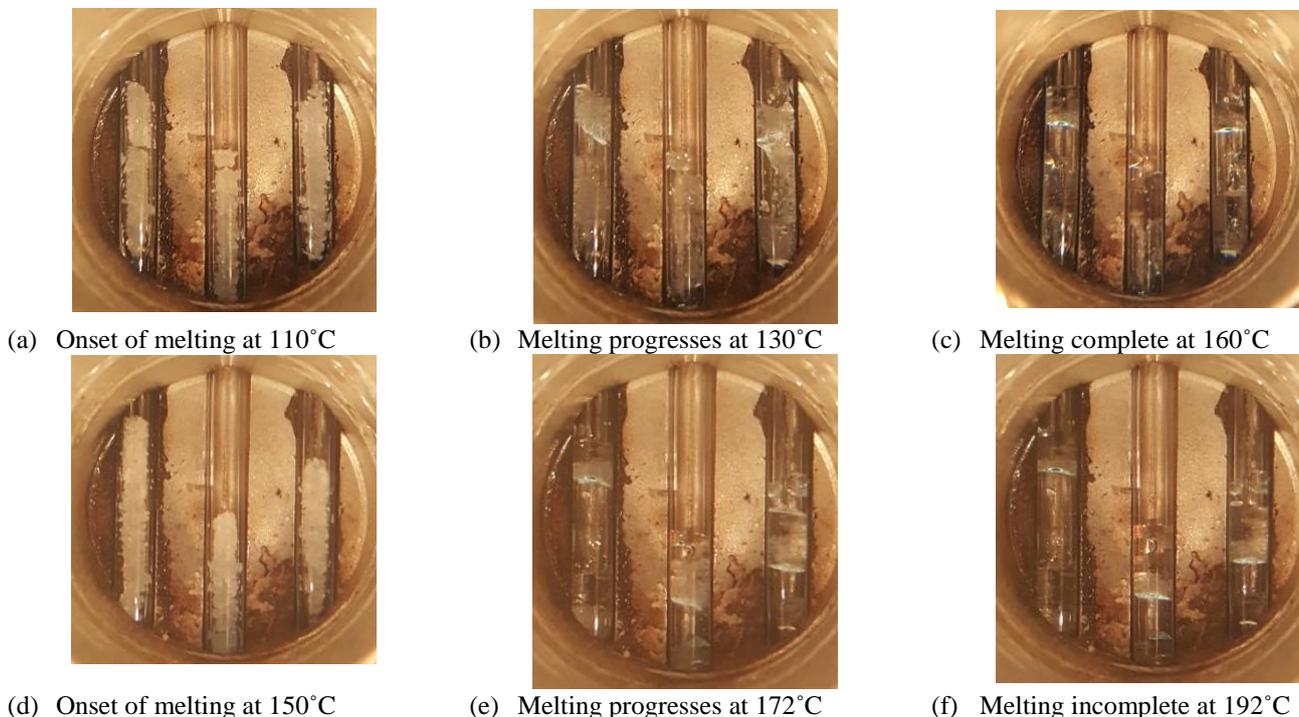


Figure 2 - Example of melting temperature field of view images in case of a successful test (a-c, LiNaK-5) and in a discontinued test (d-f, HITEC-8)

Table 4 details the composition of the 13 alternative new molten salt mixtures, their average volumetric heat capacities between 100-400°C and the experimentally identified melting point. Also included are the, variation in volumetric heat capacity and melting temperature compared to the respective baseline commercial molten salts. It can be noted that, most of the alternative salt mixtures with different compositions and higher values of volumetric heat capacities (10-24%) also resulted in a noticeable increase in the melting point temperature (62-107°C) with respect to the baseline mixtures. Whereas, the alternative salt mixtures with similar compositions resulted in a compromised solution, with small increases in volumetric heat capacities (1-15%) and melting point temperature (17-46°C) with respect to the baseline mixtures. More importantly, two alternative mixtures (CaLiNaK 11 and 4), which were associated with higher c_v improvements (15-19%), were identified to give a preferred trade-off, resulting in only moderate increases in melting point temperature (20-30°C) with respect to the baseline mixture.

Table 4 - Summary of the 13 alternative new molten salt mixtures, including mass composition, change in volumetric heat capacity and change in experimental melting point (- means that complete melting was not observed below 200°C)

Salt Name	ID	Composition	c_v [$\frac{MJ}{m^3K}$]	Δc_v [$\frac{MJ}{m^3K}$]	T_m [°C]	ΔT [°C]	σ
HITEC	5	Different	3.32	10%	-	-	-
	8	Different	3.52	17%	-	-	-
	2	Similar	3.10	3%	162	20	5.7
LiK	4	Similar	3.31	10%	172	30	3.3
	3	Different	3.27	18%	-	-	-
LiNaK	5	Different	3.26	13%	-	-	-
	2	Similar	3.04	5%	137	17	2.3
Quaternary	25	Different	3.57	20%	175	76	2.3
	11	Similar	2.99	1%	145	46	2.5
	2	Similar	3.24	9%	160	61	3.1
CaLiNaK	4	Different	3.74	19%	95	20	7.9
	17	Different	3.88	24%	170	95	6.4
	11	Similar	3.60	15%	105	30	7.2

Figure 3 presents the trade-off map to compare the volumetric heat capacity and the melting point for all the 18 experimentally tested mixtures, with points labelled 1 referring to the baseline commercial salt mixtures. Most of the salt mixtures clustered to the left-side of the dashed line, however, the salt mixtures on the right-side of the dashed line offer a preferred trade-off, where higher c_v values are a weaker function of increasing melting temperature. This trade-off map has identified 4 new molten salt mixtures, that offer low melting temperatures and beneficial thermo-physical properties, namely CaLiNaK 4, 11 and 17, and Quaternary 25. Table 5 presents the composition of these 4 new potential salt mixtures. As a result, these molten salts must be considered as candidates for use as both thermal energy storage and heat transfer fluid in the considered applications.

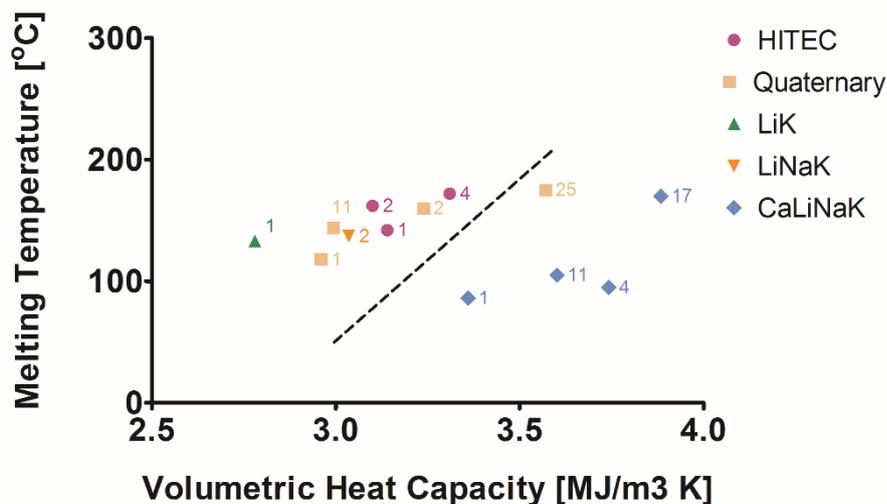


Figure 3 - Experimental melting point temperature vs. volumetric heat capacity map, for the down-selected 5 baseline commercial salt mixtures and the 13 alternative new salt mixtures

Table 5 - Composition of 4 new potential molten salt mixtures to act as both thermal energy storage and heat transfer fluid

Salt ID	Composition (wt%)
Quaternary-25	(25)NaNO ₃ , (5)KNO ₃ , (5)LiNO ₃ (65)NaNO ₂
CaLiNaK-4	(45)NaNO ₃ , (25)KNO ₃ , (5)LiNO ₃ (25)Ca(NO ₃) ₂
CaLiNaK-11	(25)NaNO ₃ , (45)KNO ₃ , (5)LiNO ₃ (25)NaNO ₂
CaLiNaK-17	(65)NaNO ₃ , (5)KNO ₃ , (5)LiNO ₃ (25)NaNO ₂

4. CONCLUSIONS

This work was focused on the identification and evaluation of low temperature molten salt mixtures as feasible common medium for both thermal store and heat transfer fluid. The parameters for evaluation were the melting point temperature and the volumetric heat capacity. Two classifications of mixtures were considered: similar compositions and noticeably different compositions to the baseline commercial salts. The significant findings of the present work are as follows:

1. Nitrate-based salts were identified for detailed investigation as they offered higher volumetric heat capacities (2.8-3.1 vs. 1.7-2.1 MJ/m³K) and comparable average melting point temperatures (113 vs. 108 °C) with respect to chloride-based salts.
2. The considered experimental procedure provided low variation in melting point temperature against the published literature. For example, HITEC, LiK and LiNaK results were reproduced within 1-3°C.
3. Experimental investigations identified the melting point of 13 alternative new molten salt mixtures in the range of 95-175°C (Table 4).
4. 4 alternative new molten salt mixtures, including 2 from the CaLiNaK family (CaLiNaK 11 and 4), were identified as preferred candidates due to higher improvements in volumetric heat capacity (15-19%) and only moderate increases in melting point temperature (20-30°C) with respect to the baseline mixture.

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