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The Effects of Nanoparticles on the Specific Heat Capacity of Molten Salts

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Abstract: The desire to increase the efficiency of existing renewable energy sources has been thoroughly researched over the past years. This meta study aimed to investigate existing methods used by previous researchers to increase the Specific Heat Capacity of Molten Salt used for Concentrated Solar Power Plants. Investigations into nanoparticles were explored because of the effect of particle size and concentration can potentially increase the specific heat capacity of the molten salt. Numerous nanoparticles have shown to improve the thermal properties such as Silica (SiO_2), Alumina (Al_2O_3), Titania (TiO_2). Our summation was that the addition of nanoparticles into Molten Salts shows an increase in desired thermal properties of the Molten Salts. An efficiency increase of up to 28% was noted in the SHC (C_p) of the Molten Salts when Nanoparticles of 60nm were introduced.

Keywords: molten salt; specific heat capacity; nanoparticles; concentrated solar power, titanium dioxide

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Nomenclature

SHC (C_p)	**Specific Heat Capacity**
CSP	**Concentration Solar Power**
Wt %	**Weight Percentage Concentration**
TiO_2	**Titanium Dioxide**
HTF	**Heat Transfer Fluid**

1. Introduction

Concentrated solar power (CSP)

In the solar energy industry, the most commonly known solar power systems are solar panels, where solar radiation is used to turn photons into electrical energy, however solar panels are not able to produce electrical energy at night, this causes a lack of energy production at night which needs to be supplemented with conventional energy sources. Concentrated solar power (CSP) is a type of renewable energy that uses solar energy to achieve energy production. Unlike solar panels, CSPs systems work by collecting heat, through reflectors which heats up a Heat Transfer Fluid (HTF) such as Molten Salts.[3] This allows the thermal energy to be transferred to secondary mediums such as water to generate steam to produce electrical energy through a turbine.[2] In addition to using Molten Salts as the HTF, Molten Salts have the ability to store thermal energy, which allows for continuous operations even when no direct sunlight is available.[8] This gives CSP an advantage over solar panels in energy generation.

Nanoparticles

Developing technology at the nano-scale opens possibility to new realms of research. As the world moves into renewable energy sources, new studies into nanoparticle size (typically between 1 and 100nm) and their effect upon properties of materials has been closely investigated. [24-29] Engineered nanoparticles (ENPs) normally possess new or enhanced physico-chemical properties compared to that of the bulk material due to inherent quantum size effects, a large surface to volume ratio, and controlled particle shape and surface coating. [1]

Molten salts

Molten Salts also known as Solar Salts are commonly a binary mixture of sodium and potassium nitrate. [15, 31] While single salts can be used for the same purpose for HTF, the sodium nitrate has a melting point of 307^{o}C and potassium nitrate has a melting point of 333^{o}C. [31] By combining these salts in a certain mixture, the melting point can be reduced to 222^{o}C, this allows for a reduced chance of the molten salts to freeze up the HTF as it moves across the CSP. [31] The advantageous properties of molten salts also include, low toxicity, cost, vapour pressure and thermal stability when in comparison to synthetic oils. [13,15]

When Molten Salts are compared to the conventional HTF of synthetic oils, these oils generally have a maximum operating temperature of 350°C before degradation occurs, this limits the maximum operating temperature of the CSP, whereas molten salts can operate at temperatures of 565°C [31] giving the CSP a much higher heat sink during the process of heating of water into steam for the CSP system. However, with the melting point of molten salts being 300 to 500°C, this increases the chance that a freeze up could occur, relative to oils, [31] where the molten salt would begin to solidify, due to not being able to maintain an operating temperature above the melting point, this would block the molten salts from flowing across the CSP system and effectively stopping the process of heat transfer to the water steam generation system in the CSP.

Increasing the Specific Heat Capacity (SHC) of the Molten Salts would allow the Molten Salts to retain this high operating temperature, through rainy/cloudy weathers, which would allow for continuous operation of the CSP. Therefore, this meta-study aims to determine what properties of nanoparticles increase the SHC of the Molten Salts.

2. Methods

Google Scholar and PubMed were accessed through UTS Library and served as the locations of the sources retrieved for this study. Different databases were used to search for scientific papers that were used as reference for the meta-study. PubMed and Google Scholar were primarily used to search for keywords that were relevant to Molten Salt with nanoparticles. Keywords that were used were nanoparticles, molten salt, specific heat capacity, thermal storage, concentrated solar power and thermodynamics. Large quantities of papers were obtained from the search result, using different combination of the keywords were utilized to narrow down the search results to find papers that were most relevant to the topic. Reading through the various abstracts were done to determine how relevant the papers were towards the topic.

The Sources used in this meta-Study were only taken from Scientific Journals as independent papers house risks for credibility and relevance. The Articles that focused first and foremost upon Molten Salts and Nanoparticles were used as they served as the most relevant and informative. Reports that were backed by Universities and large number of citations were preferable as to limit the bias due to the pertinent nature of the Nanotechnology field. We also utilized this database with Journal articles that are from 2005 onwards, as these are more relevant to our meta study.

This meta-study is based solely on how nanoparticles added into Molten Salts change the SHC of the Molten Salt and does not account into cost and toxicity against conventional HTFs. Comparison between properties of the nanoparticles, which are particle size, concentration and nanolayers formed by the particles within the Molten Salts. By comparing each property to the change in specific heat of the molten salt, a relationship between how each property contributes directly to the amount of change in specific heat can be observed. This would allow for the best contributing factor between the properties looked into, to be concluded.

Because this Study doesn't focus on the manufacturing of the nanoparticles themselves we only looked at the impact the particles had upon the Molten Salts and the systems that they are introduced into.

In order to find efficiency we looked at the initial SHC of the Molten Salts systems and how this changed when differing sized particles were introduced.

Due to the nature of our analysis we found that sifting through larger amounts of papers and finding unanimous results/conclusions added to the comprehensive nature of this Meta-Study and allowed for our conclusions to be made with high certainty.

3. Results and Discussion

Nanolayers

The addition of nanoparticles in Molten Salts have shown to increase the SHC. It was observed that there were multiple factors that contributed to what specific property of the nanoparticle would lead to the enhancement of the C_p of Molten Salts. One common explanation that has shown to be consistent throughout the various papers was the formation of Nano-layers being the key factor for the rise in C_p observed. [5-6, 13-14, 16] Nano-layers occurs at the interface of the liquid salt and solid nanoparticles, where the production of layers would be the consequent of the Molten Salts ions being constrained into a semi-solid phase. [13] Lasfargues. M, Bell. A, Ding. Y. (2015) theorized that the shape of the nanoparticles would greatly affect the adsorbed layers of fluid or solvent molecules with Nano-scale thickness. They concluded that the partial incorporation of the enthalpy of fusion in the semi-solid structure could be a viable explanation to the rise in C_p. [13]

Using this concept, Lasfargues. M, et al, (2016) hypothesized that during the liquid phase of the Molten Salts, interaction between the ionic liquid and the solid nanoparticles can enhance the SHC through the production of Nano-layers. This concept is further elaborated as it was concluded that the layer has higher thermal properties compare to the bulk liquid, which allows for the enhancement of the specific heat for nanofluids. [6,13,14]

Particle Size/Surface Area

Improving the SHC could be associated with the highly specific energies related to the high surface area of the nanoparticles per unit volume. [6] It was theorized that the diameter of the nanoparticles could play an essential role in increasing the SHC [6,7], this was achieved due to smaller nanoparticles being able to give greater solid/liquid interface area, resulting in an increasing contribution to the interfacial effect in the corresponding suspensions. [6] Changing the solid/liquid interfacial changes the phonon vibration mode near the surface area of the nanoparticle, allowing it to be able to change the SHC of a nanofluid. [6] The highly specific interfacial area of the nanoparticle is capable of absorbing liquid to the molecule's surface, forming liquid layers. [6] The layers formed were capable of constraining the nanoparticles and control the free-boundary surface atoms into non-interior atoms. [6]

It was observed that decreasing the size of the nanoparticles was able to increase the SHC of the solar salt with nanomaterials in both solid phase (Table 1, Table 3) and liquid phase (Table 2, Table 4) [8], this was supported when it was suggested that larger nanoparticles have smaller SHC which would decrease the SHC of the molten salt overall. [16]

Table 1: Enhancement of SHC with different sizes of nanoparticle in a solid phase. Values obtained from Dudda, B and Shin, D. 2013

Cp (kJ/kg C)	Solar Salt	Nanomaterial 5nm	Nanomaterial 10nm	Nanomaterial 30nm	Nanomaterial 60nm
Average(kJ/kg C)	1.21	1.25	1.26	1.27	1.34
Enhancement	-	3%	3%	5%	10%
Standard Deviation	0.02	0.04	0.04	0.04	0.04

Table 2: Enhancement of SHC with different sizes of nanoparticle in a liquid phase. Values obtained from Dudda, B and Shin, D. 2013

Cp (kJ/kg C)	Solar Salt	Nanomaterial 5nm	Nanomaterial 10nm	Nanomaterial 30nm	Nanomaterial 60nm
Average(kJ/kg C)	1.47	1.59	1.62	1.72	1.80
Enhancement	-	10%	13%	21%	28%
Standard Deviation	0.02	0.03	0.05	0.02	0.06

They were able to conclude that the increase in SHC was a result from the solar salt being able to form small nanostructure near the nanoparticles, this would effectively increase the surface area compare to the bulk material. [8] However, Tiznobaik, H and Shin, D. 2012, observed that the increase of the SHC observed was independent of the different nanoparticle size, they have observed that the solar salt would increase about 25% regardless of the size (Table 3, Table 4). [19] Tiznobai, H and Shin, D. 2012, were able to observe needle like structures forming over the nanomaterial which contributed to increasing the surface area when compared to the bulk material. (Figure 1) [19]

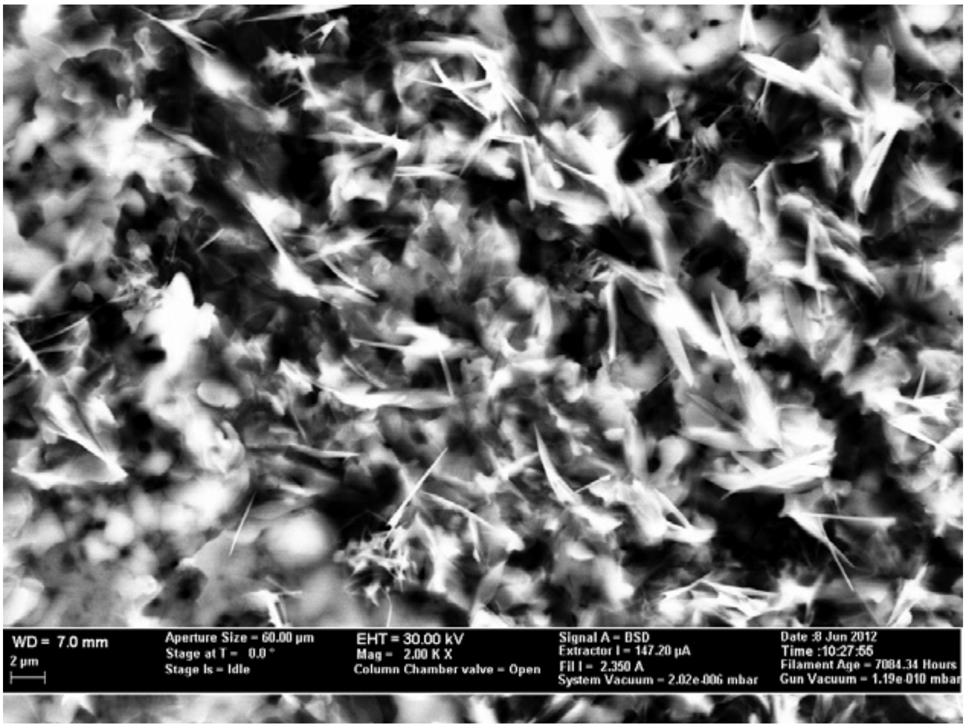

Figure 1: Backscattered electron micrograph of nanomaterial. Figure shows the Needle-like structure being brighter than the bulk salt. [19]

They had two explanations for the effects of reducing particle size had, on SHC. The first explanation was that reducing the particle size would increase the SHC surface area, this would affect the surface energy on the effective SHC. The second explanation is that since nanoparticles have very large surface area, the specific interfacial area between the nanoparticle and the surrounding solar salt are also large. This would also greatly increase the effect of the interfacial thermal resistance between the nanoparticle and the salt molecules. The interfacial thermal resistance would act as additional thermal energy storage which would increase the SHC of the nanomaterial. [19]

Table 3: Enhancement of SHC with different sizes of nanoparticle in a solid phase. Values obtained from Tiznobaik, H, Shin, D. 2012,

Cp (kJ/kg C)	Solar Salt	Nanomaterial 5nm	Nanomaterial 10nm	Nanomaterial 30nm	Nanomaterial 60nm
Average(kJ/kg C)	1.25	1.56	1.61	1.54	1.60
Enhancement	-	25%	29%	23%	28%
Standard Deviation	0.06	0.90	0.13	0.05	0.01

Table 4: Enhancement of SHC with different sizes of nanoparticle in a liquid phase. Values obtained from Tiznobaik, H, Shin, D. 2012,

Cp (kJ/kg C)	Solar Salt	Nanomaterial 5nm	Nanomaterial 10nm	Nanomateria l 30nm	Nanomateria l 60nm
Average(kJ/kg C)	1.59	1.97	2.01	1.95	2.00
Enhancement	-	24%	26%	23%	26%
Standard Deviation	0.05	0.70	0.10	0.07	0.03

Concentration

From Figure 2 that 1wt% of TiO2 was the optimal concentration to obtain the highest C_p percentage increase. Different types of nanoparticles were also tested with the molten salt and it was found that 1wt% of nanoparticle also obtained the highest value for C_p. [4, 6, 9] Although most of the results from figure2 are in the negative region, it should be noted that at 1wt%, the results are closer towards the positive region, this would further support that 1wt% of TiO_2 is the optimal concentration.

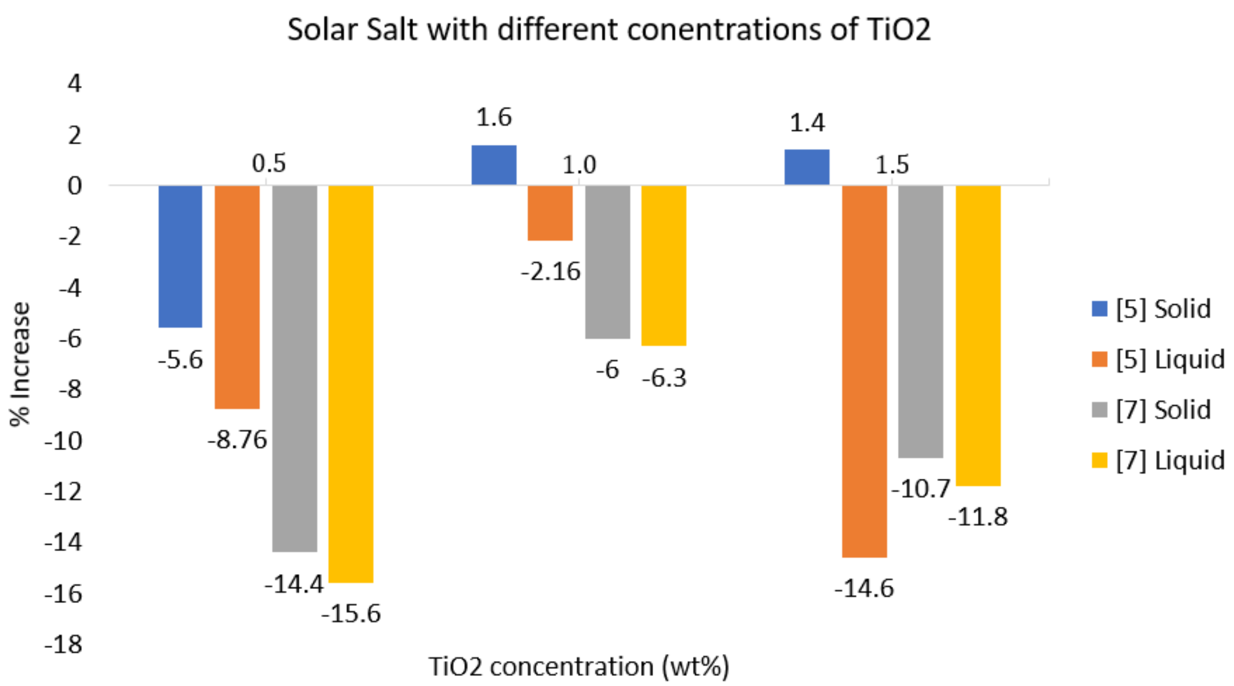

Figure 2: Effects of different concentration of TiO2 in Solar Salt

As opposed to Figure 2, Increasing the concentration of the nanoparticle decreases the SHC of the Molten Salt. [9, 14, 16] For given nanoparticle concentration, the nanolayer effect increases as the size of the particle decreases since the number of particles increases with the decreasing particle size. As a result, the SHC decreases as the particle size decreases and particle concentration increases due to the augmentation of the nanolayer effect [16]. This was also supported by Lasfargues, M. et al, 2015. [14, 16] They were able to conclude that the SHC of the molten salt was independent of the concentration of the TiO_2. [14]

In conclusion, the effect of the concentration of the nanoparticle on the solar salt affects the SHC of the solar salt, with 1wt% of TiO_2 being able to provide the greatest increase. It should be noted there were findings that suggest that the concentration of the nanoparticle was not significant enough to affect the SHC of the solar salt. [16] Therefore, further research is required to accurately determine the effect of the concentration of the nanoparticle has on the molten salt.

4. Conclusions

In this Meta-Study, Molten Salts have a singular purpose in solar power technology; to replace conventional synthetic oils currently used throughout most solar power energy generation facilities. Upon investigation into molten salt technology, and from this Meta-Study we can say that utilizing nanoparticles within Molten Salts warrants enough of a SHC increase that further study and investigation is required. An increase of 28% in the SHC of the fluid phase [28] is more than enough to increase study within this area.

Adding nanoparticles to the molten salt was shown to increase efficiency within the system. The main reason for this was the formation of Nano-layers which was the reason for the SHC to increase. TiO2 was the most commonly used nanoparticle due to its relatively low cost and high malleability.

In the solar energy industry increasing the SHC means to increase efficiency within the Solar Cell System itself and because this technology is inefficient at the moment, any optimization of any magnitude is highly sought after and the potential for growth is high. Due to these factors, it is recommended that, further research should be focused onto how the mechanics of how Nanolayers within the Molten Salts increases the SHC.

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